ENHANCING WATER BASED DRILLING FLUID PERFORMANCE USING POLYMERS AND NANOPARTICLES

BY

Hafiz Mudaser Ahmad

A Thesis Presented to the
DEANSHIP OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CHEMICAL ENGINEERING

DECEMBER 2017

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN- 31261, SAUDI ARABIA

DEANSHIP OF GRADUATE STUDIES

This thesis, written by **Hafiz Mudaser Ahmad** under the direction of his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN CHEMICAL ENGINEERING.**

Dr. Mamdouh Ahmed Al-Harthi
(Advisor)

Dr. Mohammed Ba-Shammakh
Department Chairman

Dr. Muhammad Shahzad Kamal
(Co-Advisor)

Dr. Salam A. Zummo
Dean of Graduate Studies

Dr. Abdulhadi Al-Juhani
(Member)

26/4/2018
Date

Dr. Mohammead Mozahar
(Member)

Dr. Umer Zahid
(Member)

Dedication

To my family, specially

to my mother for her ongoing love and support

and to my father who could not see this thesis completed

ACKNOWLEDGMENTS

IN THE NAME OF ALLAH THE MOST MERCIFUL AND BENEFICENT

First, I'd like to thank ALLAH Almighty, the most merciful and compassionate for HIS support, help and generosity.

Now, I would like to express my deep gratitude and appreciation to my advisor Professor Dr. Mamdouh Ahmed Al Harthi and Co-advisor Dr. Muhammad Shahzad Kamal for their tremendous mentorship for me. Their continuous support, motivation, patience and immense knowledge towards research tuned me a lot during my MS studies. Their guidance for managing experiments and writing research articles during my research helped me a lot to polish me towards research career. I am also thankful to my committee members, Dr. Abdulhadi Al-Juhani, Dr. Mohammead Mozahar Hossain and Dr. Umer Zahid for their insightful comments and encouragement.

I appreciate Mr. Lionel Tally from the research institute, Mr. Sarath P. Unikrri from chemical engineering department and Mr. Mobeen from petroleum engineering department for their support for preparing samples and characterizing the samples.

Conclusively, I acknowledge my deep gratitude to KFUPM, Department of Chemical Engineering, Centre for Investigative Petroleum Research, Centre of Engineering Research and Department of Petroleum Engineering for proving support and facilitating me during research. Finally, I would like to express my deep gratitude to my family and friends for their constant support and encouragement to complete my graduate studies at KFUPM.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

k : Consistency index

n : Flow behaviour index

m : Cross model parameter

η_0 : Zero shear rate viscosity

η_∞ : Infinite shear rate viscosity

K : Consistency coefficient

τ_0 : Yield stress

G' : Storage modulus

G'' : Loss modulus

$\dot{\gamma}$: Shear rate

R^2 : Coefficient of determination

ABSTRACT

Full Name : [Hafiz Mudaser Ahmad]

Thesis Title : [Enhancing water based drilling fluid performance using nanoparticles and polymers]

Major Field : [Chemical Engineering]

Date of Degree : [December/2017]

Water-based drilling fluids are utilized to carry out efficient and smooth drilling operations of oil and gas wells. Bentonite dispersion (base mud) was prepared to understand fundamental drilling fluid rheological properties using rheometer. Rheological data were fitted to four different classical models (Bingham plastic and Herschel-Bulkley models, Cross and Carreau models) to study the rheological behavior (Viscosity, yield point and gel strength) of bentonite dispersions. XRF and XRD were used to study the chemical and mineral composition of the bentonite. In the second part, impact of molecular structure such as the degree of hydrolysis (DOH) and nature of comonomers in acrylamide-based copolymers on the rheological and filtration properties of bentonite dispersions was assessed using three different water-soluble polymers for water-based drilling fluids. These polymers are, copolymer of acrylamide and 2-acrylamido-2-methylpropane sulfonic acid (AMPS) with 10% DOH, copolymer of acrylamide and 2-acrylamido-2-methylpropane sulfonic acid with 25% DOH, and copolymer of acrylamide and acrylic acid with 15% DOH. Steady shear rheology data was fitted to the Herschel-Bulkley model and flowability test was performed at 25°C and 85°C. Aging of bentonite and bentonite/polymer dispersions was performed at 90°C for 16 hours. Results showed that the incorporation of polymers in bentonite enhanced the filtration and rheological properties. The

bentonite/polymer dispersion showed better rheological properties compared to other bentonite dispersions. The better rheological properties of bentonite/polymer dispersion suggest that acrylamide-based copolymers containing smaller comonomers such as acrylic acid are better compared to the bulky comonomers such as AMPS for drilling fluids applications. In the third part, the combined addition of nanoparticles (TiO_2, ZnO) and an associative polymer to the base drilling fluid significantly reduced filtrate volume, improved filter cake permeabilities and thickness. The incorporation of nanoparticles and polymer resulted in superior rheological properties such as improved viscosity, yield point and gel strength.

ملخص الرسالة

الاسم الكامل: حافظ مدثر احمد

عنوان الرسالة: تحسين أداء المياه المستندة إلى فلويد الماء باستخدام البوليمرات و نانوبارتيكلس

التخصص: هندسة كيميائية

تاريخ الدرجة العلمية: ديسمبر/٢٠١٧

وتستخدم سوائل الحفر القائمة على المياه لتنفيذ عمليات حفر آبار النفط والغاز بكفاءة وسلاسة. تم إعداد تشتت البنتونيت (قاعدة الطين) لفهم خصائص الحفر الأساسية السوائل الريولوجية باستخدام مقياس الحرارة. تم تركيب البيانات الريولوجية على أربعة نماذج كلاسيكية مختلفة (نماذج بينغهام البلاستيكية و هيرشل-بولكلي، كروس و كاريو) لدراسة السلوك الريولوجي (اللزوجة، نقطة الغلة وقوة هلام) من البنتونيت التشتت. تم استخدام زرف و زرد لدراسة التركيب الكيميائي والمعدني للبنتونيت. في الجزء الثاني، تم تقييم تأثير التركيب الجزيئي مثل درجة التحلل المائي (دوه) وطبيعة كومونوميرس في البوليمرات القائمة على الأكريلاميد على خصائص الريولوجية والترشيح من البنتونيت تشتت باستخدام ثلاثة بوليمرات مختلفة للذوبان في الماء للحفر المياه القائمة السوائل. هذه البوليمرات هي، البوليمرات من الأكريلاميد و 2-أكريلاميدو-2-ميثيلبروبان حمض السلفونيك (أمبس) مع 10٪ دوه، البوليمرات من الأكريلاميد و 2-أكريلاميدو-2-ميثيلبروبان حمض السلفونيك مع 25٪ دوه، وكوليمر من الأكريلاميد وحامض الاكريليك مع 15٪ وزارة الصحة. تم تركيب بيانات الريولوجيا القص الثابتة لنموذج هيرشل-بولكلي وتم إجراء اختبار قابلية التدفق عند 25 درجة مئوية و 85 درجة مئوية. تم تنفيذ شيخوخة البنتونيت والبنتونيت / تشتت البوليمرات في 90 درجة مئوية لمدة 16 ساعة. وأظهرت النتائج أن دمج البوليمرات في البنتونيت يعزز الترشيح وخصائص ريولوجية. أظهر البنتونيت / تشتت البوليمر أفضل خصائص ريولوجية مقارنة مع غيرها من البنتونيت التشتت. أفضل خصائص ريولوجية من

البنتونيت / تشتت البوليمر تشير إلى أن البوليمرات القائمة على الأكريلاميد التي تحتوي على كومونومرات أصغر مثل حمض الاكريليك هي أفضل بالمقارنة مع كومونوميرس ضخمة مثل أمبس لتطبيقات سوائل الحفر. في الجزء الثالث، إضافة الجمع بين الجسيمات النانوية (TiO2، أكسيد الزنك) والبوليمر الارتباطية إلى السائل قاعدة الحفر بشكل كبير خفض حجم الترشيح، وتحسين نفاذية كعكة مرشح وسمك. أدى دمج الجسيمات النانوية والبوليمر إلى خصائص ريولوجية متفوقة مثل اللزوجة المحسنة ونقطة الغلة وقوة الهلام

CHAPTER 1

Introduction and objectives

1.1 Introduction

In the exploration and extraction of oil and gas, the first step is drilling of well bore using drill bit. To assist in smooth and easy drilling process drilling fluids are employed. Drilling fluids are also called drilling muds. The basic functions of drilling fluids are: stability control of well bore, remove the rock cutting from the borehole to surface and cleaning of well, to control pressure, to cool and lubricate the drilling bit, overcome the friction between drilling pipe and borehole walls, to control formation pressure and to block pores in the shale to prevent fluid loss. Conventional drilling process is easy and cheap as compared to unconventional drilling process. Conventional drilling includes the drilling of well and oil comes out with its own pressure. After that pump jack is employed at the oil well to take out further oil from the well. While unconventional drilling process includes horizontal drilling of wells which also includes special treatment such as the injection of chemicals (polymer solutions along with additives) into the well that enhance the productivity of oil well [1].

Conventionally three types of drilling fluids are used for drilling oil wells. Such as: pneumatic air, water based drilling fluid (WBDF) and oil based drilling fluids (OBDF). But most commonly WBDF fluids are employed for drilling process. Around 5-10% drilling process is carried out by OBDF and 80-90% drilling is done using WBDF. In WBDF, fresh water is used along with different types of salts such as potassium chloride (KCl), sodium carbonate (Na_2CO_3) which are beneficial for shale

inhibition for sensitive shale formations. Many water-soluble polymers are also used in addition of WBDF. Such as natural polymers which include starch (to prevent fluid loss circulation), polysaccharides which include guar gum (which tailor the rheology of drilling fluid), xanthan gum and synthetic polymers include polyacrylamide and polyacrylate which has high molecular weights used to stabilize shale in oil well [2].

Several types of additives are utilized in drilling fluid to enhance physical, chemical, rheological and filtrate loss properties. These additives include weighting materials (barite, hematite, calcium carbonate, $BaSO_4$) to increase the density of drilling fluid and to control the thickness of filter cake around well [3], rheological properties such as viscosity is controlled by (smectite clay) [4] and other polymers such guar gum, xanthan gum, polyacrylamide, polyanionic cellulose, sodium carboxymethyl cellulose (Na-CMC) [5], nanoscale additives such as (Nano silica, CuO, ZnO) are used to reduce fluid loss, formation control and smooth drilling operation [6, 7], lubricity control additives are employed to control the friction between wellbore and pipelines for smooth operation such as (vegetable oils, polyols i.e. polypropylene glycol), stabilizing agents are added to drilling fluids to improve the performance at high temperature and pressure at downhole conditions of oil well such as (zinc oxide nanoparticles, multiwall carbon nanotube MWCN, silica nanoparticle) [8]

Based on the types there are three types of drilling fluid. Pneumatic air, water based drilling fluid (mud) and oil based drilling mud. Pneumatic air has very little use in drilling wells where the wells are shallow in nature and have competent formations. Oil based drilling muds are employed only 5-10 % because of environmental regulations and constraints and relatively excessive cost as compared to water based drilling fluids. The use of water based drilling muds are more desirable as compared to other drilling fluids due to less operations cost and capital cost [2].

1.2 Objectives

1. To study the effect of concentration of bentonite, polymers, nanoparticles and electrolyte on rheological properties of drilling fluids using DHR-3 rheometer.

2. To study the combined effect of bentonite, polymer and nanoparticles on rheological properties of drilling fluids

3. To study the effect of temperature on rheological properties of prepared drilling fluids

4. To study the characteristics of bentonite with x-ray florescence analysis (XRF), x-ray diffraction analysis (XRD), Fourier transform infrared spectroscopy (FTIR) and thermal gravimetric analysis (TGA)

5. To measure the filtration properties of drilling fluids using filter press apparatus to overcome fluid loss into formations

6. To determine thermal stability of drilling fluid after aging in hot air oven for 16 hours at specified temperature

CHAPTER 2

LITERATURE REVIEW

2.1 Bentonite in drilling fluids

Bentonite dispersions are used in multiple industrial applications such as emulsion stabilization, adhesives, industrial absorbents, cement, cosmetic, sealants, water clarification, and most importantly in water-based drilling muds [9]. Bentonite formed by weathering effect on volcanic ash mainly consists of montmorillonite (Mt) with different composition of other minerals such as quartz, sodium, and calcium feldspar [10]. The physical and chemical properties of clay typically depend on the composition, structure, particles size, surface area, ion exchange capacity, absorption, and swelling capacity [9]. Na-bentonite has a high swelling capacity and Ca-bentonite has less swelling capacity upon hydration with water [11]. A single unit cell of montmorillonite (Mt) has two sheets of tetrahedral silica and in between these sheets, there is an octahedral sheet of alumina. Many unit cells are stacked over each other giving the layered structure of clay [12]. The surface of layers carries negative charge due to the isomorphic replacements of cations within the structure and these ions are responsible for balancing the negative charge on surfaces [13]. These cations are known as exchangeable cations, which are accountable for physical properties and clay swelling in water. The most common cations available are sodium, aluminum, potassium, and calcium along with many less common ions which include iron and titanium. The layered structure of bentonite has the capacity to adsorb water molecules in between the layers and resulting in the increase in swelling by increasing the c-axis dimension of clays [14]. This swelling capacity of bentonite makes it a suitable candidate for drilling fluids as viscosifier to customize the rheological properties.

Water based drilling muds specially bentonite-water dispersions are of immense importance to the oil & gas industry and being used worldwide due to its unique and excellent swelling and gel formation properties [15, 16]. The basic functions of drilling muds are: to control stability of well bore, to remove the rock cutting from the borehole to surface, to cool and lubricate the drilling bit, to overcome the friction between drilling pipe and borehole walls, and to block pores in the shale to prevent fluid loss [17-19]. Rheological properties of bentonite dispersions such as plastic viscosity, apparent viscosity, gel strength, and yield stress are very important for drilling fluids. These properties mainly governed by the associations among the particles of bentonite [20, 21].

There are three types of associations among the bentonite particles in aqueous dispersions namely face to face, edge to edge and face to edge [3, 22]. Edge to edge and face to edge association form a three-dimensional network similar to a card house structure and face to face association forms a band structure in bentonite dispersions [16]. The gel formation in bentonite dispersions is because of two mechanisms; first is the strong electrostatic force of attraction between positively charged edges and negatively charged surfaces. The second mechanism is edge to edge and face to face interactions through double layer repulsion among the particles [15, 23]. These associations are accountable for customizing the rheological properties of bentonite dispersions and these associations are incredibly affected by concentration and type of electrolytes, temperature, and concentration of bentonite.

All the bentonite dispersions in deionized water show shear thinning rheological behavior [3, 24]. This phenomenon is associated with the change of inter-particles interactions. At low shear rates, due to high inter-particles associations and the presence of immobilized adsorbed water inside agglomerated structure of bentonite results the increase in viscosity. While at high shear rates, inter-particle associations are disrupted with the release of adsorbed water which results in the decrease in

viscosity [23]. The presence of electrolytes mainly NaCl in water-bentonite dispersions strongly affects the rheological properties by compressing the electrical double layer, which is formed around the bentonite particles and help them to remain in dispersed form [25-27]. Several studies were reported in the literature showing the effect of electrolyte concentration on rheological properties of different bentonite dispersion [14-17, 19]. At elevated temperatures, bentonite water dispersion shows unusual behavior in rheological properties which results in thickening of dispersions. The thickening of bentonite dispersions was attributed to the formation of clusters and enhanced face-to-face interactions at high temperature, which resulted in the increase of rheological properties [27, 28]. The rheological properties of bentonite dispersions were mostly evaluated by fitting experimental data into classical drilling fluid rheological models. The variation of model parameters was evaluated to study the non-Newtonian behavior of bentonite dispersions in the presence of electrolyte with elevated temperature.

The rheological flow behavior helps us to understand the performance of bentonite dispersions in drilling applications. Here two well-known rheological models (Cross model and Carreau model) are selected for determining the applicability of experimental data [29]. These models show that at very low shear rates, viscosity and shear rate are linearly related with each other. While at high shear rates, viscosity and shear rates are not linearly related to each other. These models will explain the non-Newtonian behavior of bentonite dispersions over a wide range of shear rates. Similarly, the experimental data on flow curves obtained are fitted to Bingham plastic model and Herschel-Bulkley model to determine their applicability [30-32]. Bingham model illustrates that a threshold stress is needed to initiate the flow and after the stress, materials behave as a Newtonian fluid and it shows the best fitting of experimental data at low shear rates. While Herschel-Bulkley model explains yield stress and non-Newtonian behavior of bentonite dispersions over the wide range of shear rates.

2.2 Effect of polymers on drilling fluid properties

Drilling fluids perform vital roles in oil and gas drilling operations, such as maintaining rheological properties, cooling the drilling bit, transporting the formation cuttings from bottom hole to the surface, balancing the formation pressure, inhibiting shale dispersion, and preventing the invasion of fluid into formations [5, 33-35]. Drilling fluids are mainly classified into three categories, including oil-based drilling fluids, synthetic-based drilling fluids, and water-based drilling fluids [23, 36, 37]. Oil-based and synthetic drilling fluids are not frequently advised for drilling operations due to environmental concerns because they are health hazards and have high costs relative to the water-based drilling fluids [38]. Water-based drilling fluids are generally used worldwide to carry out drilling operations because they are environment-friendly, easy to prepare, cost-effective, safe, and most efficient compared to other drilling fluids [39-41]. Water-based drilling fluids have bentonite as a basic component to control drilling fluid properties. High concentration of bentonite in drilling fluids has various detrimental effects which include: (1) chances of pipe sticking, (2) lowering the penetration rate of the drill bit, and (3) enormous torque and drag are required for drilling operations [42, 43]. Thus, less concentration of bentonite is desired to have low solid contents in drilling fluids. However, low concentration of bentonite is unable to maintain desired rheological properties required for smooth drilling operations. Hence, various natural and synthetic polymers are employed to accomplish the desired properties of drilling fluids [44].

Natural and synthetic polymers are widely used as rheology modifiers, shale inhibitors, and fluid loss additives in water-based drilling fluids. These polymers are primarily used to control rheological properties, filtration properties and shale inhibition properties of water-based drilling fluid [45-48]. Water interacts with shale and causes swelling of shale that leads to the well bore instability problems

such as a tight hole, dispersion of shale, and bit balling [49, 50]. The water-soluble polymers in water-based drilling fluids inhibit shale swelling and fluid loss by encapsulating shale with a thin layer of polymer and prevent the invasion of water into the formation. Recently, various synthetic and natural polymers are employed in water-based drilling fluids to prevent the fluid loss into the formations and to modify rheological properties. Recently, Baba et al. have used two different biopolymers such as xanthan gum and sclera-glucan to modify rheological properties of water-based drilling fluids [51]. Jain et al. synthesized polyacrylamide grafted xanthan gum with multiwalled carbon nanotube nanocomposite to investigate the rheological properties as one of the drilling fluid additives [52]. Other polymers employed in water-based drilling fluids include starch, polyacrylates, polyacrylamide, hydrolyzed polyacrylamide, partially hydrolyzed polyacrylamide, amphoteric cellulose, polyanionic cellulose, and carboxymethyl cellulose has been used to modify rheological properties and fluid loss control agent.

The primary challenge to use natural and synthetic polymers in drilling fluids is to maintain rheological and filtration properties at high temperature- high-pressure conditions of the bottom hole. These polymers lose their rheological and filtration properties due to degradation of polymers at high temperature and high pressure at deep well conditions [43, 45, 49]. Recently, the use of high molecular weight copolymer with rigid backbone polymer chains have caught much attention for water-based drilling fluids due to their unique structure, hydrophilic functional groups, the degree of hydrolysis (DOH) and ability to bear high temperature at bottom hole [53, 54]. So, these high molecular weight polymers with distinctive functional groups could effectively control filtration and rheological properties due to their structural stability, hydrophilic functional groups along the backbone and high structural viscosity [55].

Drilling fluid execute vital roles in drilling operations which include: to transport rock cuttings to the surface, to reduce the formation damage, to cool and lubricate the drilling equipment, to maintain wellbore stability, to control formation pressure and to minimize fluid loss and lost circulations [5, 35, 56]. There are several types of drilling fluids such as water-based drilling fluids, oil-based drilling fluids, pneumatic drilling fluids and synthetic-based drilling fluids [23, 57]. Careful selection of drilling fluid is essential to avoid several problems like wellbore instability, formation damage, drag and torque reduction [58]. Out of all above mentioned drilling fluids, water-based drilling fluids are most recommended worldwide due to excellent performance, environment-friendly, shale inhibition capacity, easy to prepare and due to remarkable rheological properties [59, 60]. To perform successful drilling operations, the selection and quantity of drilling fluid additives are very important for the desired fluid filtration and rheological properties [61]. Bent is one of the essential constituents of water-based drilling fluid which controls the rheology of drilling fluids. High concentration of Bent in water-based drilling fluids can have detrimental effects on drilling operations which include the reduction of drill bit penetration rate, thick filter cake, differential pipe sticking and formation damage. Furthermore, elevated temperature and pressure conditions at the bottom hole results in thermal induce swelling (flocculation) of Bent [62]. Therefore, it is highly seductive to find out other additives which can compensate the Bent related problems and satisfy the desired properties of drilling fluids.

The incorporation of organic additives (polymers) in water-based drilling fluids has significant industrial importance to compensate for Bent deficiencies and to modify the fluid filtration and rheological properties [44]. Polymers in water-based drilling fluids can perform various functions such as shale inhibition, as viscosifiers, as Bent extenders and fluid loss control agent [47, 63, 64]. The interaction between Bent platelets and polymer molecules are very important which decides the

properties of Bent /polymer dispersions. It is recognized that when polymers added to clay dispersion, the interaction among clay platelets and polymers results in the adsorption of polymer chains on the surface of clay particles. This interaction among clay platelets and polymers depends on polymer structure, the chemical structure of monomer in the backbone, charge distribution in monomer groups and their distribution along the polymer chains. The clay-polymer interactions have immense importance and significant influence the rheological and filtration properties of water-based drilling fluids [65, 66].

Recently various polymers (natural and synthetic) are employed to tailor the rheological and filtration properties of drilling fluids. A variety of polymers are added into water-based drilling fluids such as polyanionic cellulose (PAC) [67], sodium carboxymethyl cellulose and xanthan gum to obtain the desired filtration and rheological properties [68]. Kunlin et al. used novel biopolymer to improve rheological properties such as gel strength, yield point and viscosity of water-based Bent drilling fluids, fluid loss characteristics and formation damage [67]. Dajun et al. used polyacrylamide/xanthan gum solution to improve the rheological properties of drilling fluids [69]. The impact of inorganic salt on drilling fluid properties showed that the presence of high concentration of salts severely affects the viscosity and drilled cutting lifting capacity [70]. Many other polymers such as cellulose, polyacrylates, starch, partially hydrolyzed polyacrylamide (PHPA), polyacrylamide (PAM), hydrolyzed polyacrylamide (HPAM), polyanionic cellulose, and carboxymethyl cellulose (CMC) were used to study the rheological and filtration properties of water-based Bent drilling fluids.

The basic challenge to use conventional synthetic and natural polymers as drilling fluid additive at the harsh condition of elevated temperature and pressure at bottom-hole severely affects the

rheological and filtration properties [43, 49]. In this study, two different anionic polymers (copolymer and terpolymer) are employed as water-based drilling fluid additive. The copolymer has two monomers which include acrylamide and 2-acrylamido-2-methylpropane sulfonic acid monomers in its structure. The copolymer structure is thermally stable up to 95°C and can bear high salinity environment. Terpolymer has three monomers which include acrylamide, 2-acrylamido-2-methylpropane sulfonic acid, and N-Vinylpyrrolidone. Terpolymer has additional N-Vinylpyrrolidone monomer which has high thermal stability up to 120°C and can bear harsh salinity environment [71].

2.3 Effect of polymers and nanoparticles on drilling fluid properties

Drilling fluids are widely used for the drilling of new and mature reservoirs to explore the oil and gas reserves and to extract the fossil fuels from underground. The main functions of drilling fluid include to maintain the rheology, to minimize the fluid loss, minimize the formation damage, to cool and lubricate the drill bit and well bore stability [24, 50, 52, 72, 73]. Various additives for water base drilling fluids are utilized such as viscosifiers, rheology control agents, filtration control agents, pH control agents, density control agents and shale inhibitors [74, 75]. The most important properties of drilling fluids include rheology and filtration properties. To enhance rheology of water based drilling fluid, various polymers and nanoparticles are being employed [76-79].

The polymers used for water based drilling fluid additives include hydrolyzed polyacrylamide, xanthan gum, guar gum, polyvinyl alcohol, and partially hydrolyzed polyacrylamide. The nanoparticles are also being utilized for the improvement of rheological and filtration properties of drilling fluids. Nanotechnology has many uses in various industries such as cosmetics, electronic and medicine industry. Nanoparticles are those material which have at least one dimension in nano meter

scale. Currently, various types of nanoparticles are utilized for the enhancement of drilling fluid properties and performance. Cellulose nanoparticles are utilized for increase the rheological and filtration properties of drilling fluids. Silica nanoparticles are used to improve the filtration characteristics of drilling fluids. There are micro or nano pores in the formation of well bore. The small nanoparticles are utilized to plug the cracks and pores in the well bore formation. These nanoparticles prevent the invasion of drilling fluid into the formation usually in the production zone[34, 44, 80-83].

Drilling fluids are widely used to assist in drilling operations for the exploration of natural resources [84]. Water-based drilling fluids (WBDF) are a complex mixture of multi-components in which bentonite clay is dispersed homogeneously as a continuous phase [25]. Other components typically include barite as a weighting material, polymer as a viscosifier and a shale inhibiting agents, salts, pH control agents, and nanoparticles as fluid loss material [3, 52, 85-87]. The functions of WBDF in drilling operations are to maintain the column pressure against the formation pressure, to transport the formation cuttings to the surface, to maintain the viscosity during drilling operations, shale inhibition and to prevent the loss of drilling fluid into the reservoir formations [1, 43, 88]. In addition to these function, WBDF must be environment-friendly, non-corrosive, cheap and less reactive, and have superior temperature and salt tolerance [89]. The most important constituent of WBDF is bentonite clay which acts as a viscosifier in drilling operations. Bentonite clay mainly composed of sodium montmorillonite which represents some unique properties such as swelling upon hydration, thixotropy, and cake formation [16]. It also represents cation exchangeability and low permeability when in the wet state [12]. Bentonite dispersions are impermeable in a stable state which makes it a suitable candidate for drilling fluids. Bentonite clay has a layered structure in which octahedral sheets of alumina is sandwiched between two tetrahedral sheets of silica [90, 91]. The interlayer cations are

responsible for holding these sheets together by the electrostatic force of attraction. When bentonite clay hydrated with water, the exfoliation of inter-layer occurs which leads to the adsorption of water on negatively charged surfaces [92]. The adsorption of water and particle to particle associations leads to the increase in rheological behaviour of bentonite [18]. But the use of bentonite dispersion alone as a potential drilling fluid may cause some serious problems. It makes a thick filter cake on the formations which lead to the potential pipe sticking, formation damage, and lowering the drilling operation productivity [56, 93]. To overcome these problems, polymer-clay based drilling fluids with attractive rheological properties are normally used [23].

Recently, various natural and synthetic polymers are utilized to modify the rheological and filtration properties of drilling fluids such as xanthan gum [94], guar gum [95], starch, polyanionic cellulose [96], carboxymethyl cellulose [97], polyacrylamide [98], hydrolyzed polyacrylamide, and polyacrylates [52]. A recent study represents the effect of polyanionic cellulose and tamarind gum on the rheological and filtrations properties of WBDF. The results exhibit the enhanced rheological properties, reduction in fluid loss volume, and excellent stability of shale formation and wellbore [99]. Alternatively, the use of nanoparticle also improves the performance of drilling fluids. Previous studies showed that nanoparticles in drilling fluids help in plugging micropores in formations and reduces the permeability of shale. The presence of nanoparticles in drilling fluid reduces the fluid loss into the formation and forms a thin filter cake [31, 100]. The use of polymers and nanoparticles in combination presents the synergistic effect with the improved rheological properties and less fluid loss volume.

All WBDF represents the non-Newtonian behaviour, therefore, the rheological behaviour of drilling fluids is interpreted by different rheological models [101]. The most widely used models to explain drilling fluid rheological properties are Bingham plastic model, Herschel-Bulkley model and Casson

fluid model [102-104]. The important rheological parameters that explain the non-Newtonian rheological behaviour of drilling fluids are yield stress, plastic viscosity, and flow behaviour index. Yield stress (the minimum amount of stress required to initiate the flow) is the most important parameter for determining the drilled cutting transport capacity to the surface. The plastic viscosity is resistance to flow of drilling fluid during the drilling operation and its low value will represent the smooth drilling process. The flow behaviour index describes the nature of drilling fluid such as $n=1$ indicates Newtonian behaviour, $n<1$ show shear thinning non-Newtonian behaviour, and $n>1$ represents the shear thickening non-Newtonian behaviour [105-107]. These model parameters describe the insight information about rheological properties and the selection of suitable drilling fluid.

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Experimental Procedure

3.1.1 Materials

Bentonite (BT) was obtained from BDH Chemicals (UK) with a density of 2.5 g/cm^3 at 20°C and a pH ranges from 9.5-10.5. Sodium chloride (S) salt used in this study was obtained from Sigma-Aldrich with purity ≥99%. Various high molecular weight copolymers were obtained from SNF FLOERGER. The polymer P is an associative polymer which has hydrophilic and hydrophobic moieties with 10 million g/mol molecular weight. The polymer P1 is a copolymer of acrylamide and 2-acrylamido-2-methylpropane sulfonic acid (AMPS) with 10% DOH. The polymer P2 was a copolymer of acrylamide and 2-acrylamido-2-methylpropane sulfonic Acid with 25% DOH. The polymer P3 was a copolymer of acrylamide and acrylic acid with 15% DOH. All the three copolymer has 9 million g/mol molecular weight. The polymer P4 is a terpolymer of acrylamide (AM), 2-acrylamido-2-methylpropane sulfonic acid (AMPS) and N-Vinylpyrrolidone (NVP). Various nanoparticles were used in this study which are obtained from Fisher Scientific and Cheap tubes Inc. such as TiO2 (N1) and ZnO (N2) with whitish colour and 99.0% purity and functionalized single-wall carbon nanotubes (N3) having outer diameter ranges from 1-2 nm with 90 % purity. Second, graphitized multi-wall carbon nanotubes (N4) having outer diameter 8-15 nm and 99.9% purity. Caustic soda was obtained from Sigma Aldrich with solubility 1260 g/L at 20 °C. Barite (BaSO4) powder was obtained from Baroid Saudi Arabia Ltd Co.

3.1.2 Preparation of different bentonite dispersions

In the first phase, four different bentonite dispersions (4 m% to 7 m%) were prepared in deionized water by using IKA ultra-high-speed disperser for 20 minutes as per given procedure in American Petroleum Institute (API) standards. All the bentonite dispersions were left for 24 hours for the hydration of bentonite. In the second phase, four different samples of bentonite dispersions were prepared with various concentrations of electrolyte of (0.025 M - 0.1M) sodium chloride solution and 5 m% concentration of bentonite. Electrolyte solutions were prepared by mixing the desired amount of salt in deionized water All the samples were left undisturbed at room temperature for 24 hours before rheological characterization of bentonite dispersions. The pre-shearing was applied to all the dispersions before rheological experiments for 5 minutes using IKA ultra-high-speed disperser to get consistent results.

3.1.3 Preparation of bentonite/polymer dispersions

In the first phase, polymer solutions were prepared using magnetic stirrer. Each polymer solution has 0.25 wt.% concentration in deionized water. Stirring was applied for 3 hours and solutions were left undisturbed for next 3 hours for complete hydration of polymers. In the second phase, bentonite/polymer dispersions were prepared by dispersing 5 wt.% BT in deionized water using mechanical stirrer followed by mixing with 0.25 wt.% polymer solutions. In this way, three bentonite/polymer dispersions were prepared such as BT/P1, BT/P2, and BT/P3. After mixing polymer solutions with bentonite dispersions, stirring was applied for next 30 minutes for complete homogenization of the bentonite with the polymer. Then bentonite/polymer dispersions were left undisturbed for 24 hours before starting rheological experiments.

3.1.4 Preparation of bentonite/electrolyte/polymer dispersions

In the first stage, polymer solutions were prepared in deionized water and 0.1 M salt water having 0.25 m% polymer concentration with magnetic stirring. Magnetic stirring on each polymer solution was applied for 2 hours and followed by the 2 hours hydration time for complete homogenization of polymers in deionized water. In the second stage, 5 m% Bent dispersions were prepared in deionized water and 0.1 M salt water using mechanical stirrer and stirring was applied for 1 hour. The polymer solutions were mixed with Bent dispersions and mechanical stirring was applied for 30 minutes for complete mixing of Bent dispersions and polymer solutions with each other. All the Bent/polymer dispersions kept 24 hours undisturbed before rheological and filtration experiments.

3.1.5 Preparation of bentonite/nanoparticles/polymer dispersions

Six drilling fluid formulation were prepared using bentonite, polymers and nanoparticles. All the formulations, compositions and function of drilling fluid components are mentioned in Table 3.1 and Table 3.2. Bentonite dispersion (base fluid) was prepared by mixing bentonite in deionized water with speed mixer. Bentonite/nanoparticle dispersions were prepared by dispersing nanoparticles, caustic soda and barite powder in deionized water using ultra-sonication at 40°C for 30 minutes and then bentonite in the nanoparticles dispersion. Bentonite/polymer dispersion was prepared by first dissolving polymer in deionized water using magnetic stirrer and bentonite, caustic soda and barite powder was mixed in a separate beaker using mechanical mixer and left for 24 hours for the hydration of bentonite. Then, polymer solution and bentonite dispersion were mixed together and allowed to stir for 30 minutes. The bentonite/nanoparticles/polymer dispersions were prepared by first dispersing nanoparticles in deionized water using ultra-sonication and bentonite is mixed using mechanical stirrer. The mixture of bentonite and nanoparticles dispersion was left for 24 hours. The polymer solution was mixed in to the mixture of nanoparticles and bentonite dispersion along with

caustic soda and barite powder. Caustic soda was used to maintain the pH of drilling fluid while barite powder was used to increase the density of drilling fluids.

Table 3.1 Formulations of six water based drilling fluids

Materials	Formulations					
	BT	BT/N1	BT/N2	BT/P	BT/N1/P	BT/N2/P
Bentonite (g)	20	20	20	20	20	20
Nanoparticles (N1) (g)	-	0.8	-	-	0.8	-
Nanoparticles (N2) (g)	-	-	0.8	-	-	0.8
Polymer (P) (g)	-	-	-	0.4	0.4	0.4
Caustic soda (g)	0.20	0.20	0.20	0.20	0.20	0.20
Barite (g)	20	20	20	20	20	20

Table 3.2 Formulations of six water based drilling fluids

Materials	Functions
Water	Dispersion medium
Bentonite	Viscosifier
Nanoparticles (N1)	Filtration control
Nanoparticles (N2)	Filtration control
Polymer (P)	Rheology and filtration control
Caustic soda	PH control
Barite	Density control

3.2 Characterization of drilling fluids

3.2.1 Measurement of rheological properties

Rheological experiments were performed using Discovery Hybrid Rheometer (DHR-3) having concentric cylinder geometry with bob and cylinder diameter of 28 mm and 30.43 mm, respectively. The shear stress (τ) and viscosity (η) data were measured as a function of controlled shear rate ($\dot{\gamma}$)

ranging from 0.01 s^{-1} to 1000 s^{-1}. Dynamic shear experiments were performed with an angular frequency ranging from 0.1 rad/s to 100 rad/s.

Apparent viscosity, plastic viscosity, yield stress and gel strength were measured from rheological experiments. To get yield stress and plastic viscosity, experimental data were fitted to Bingham model [25]

$$\tau = \tau_o + \eta_p(\dot{\gamma}) \qquad (1)$$

Where, τ, τ_o, η_p, and $\dot{\gamma}$ are measured shear stress, yield stress, plastic viscosity, and shear rate, respectively. A three parameter Herschel-Bulkley was also used to study the rheological behavior of bentonite dispersions [31].

$$\tau = \tau_o + K(\dot{\gamma})^n \qquad (2)$$

Where K and n are consistency coefficient and flow behavior index.

Cross and Carreau models were used to study the non-Newtonian behavior of bentonite dispersions over the wide range of shear rate ranging from 0.01 s^{-1} to 1000 s^{-1}. Limiting values of viscosities were calculated at very high and very low shear rates by fitting experimental data to the following models.

Cross Model

$$\frac{\eta - \eta_\infty}{\eta_o - \eta_\infty} = \frac{1}{[1 + (k\dot{\gamma})^m]} \qquad (3)$$

Carreau Model

$$\frac{\eta - \eta_\infty}{\eta_o - \eta_\infty} = [1 + (k\dot{\gamma})^2]^{(n-1)/2} \quad (4)$$

where η (Pa.s) is viscosity at a particular shear rate $\dot{\gamma}$ (s^{-1}), η_o (Pa.s) is zero shear rate viscosity and η_∞ (Pa.s) is infinite shear rate viscosity. Other parameters of these models include consistency index k (s), rate constant (m) and flow behavior index (n).

Dynamic rheology such as amplitude sweep measurements was performed at 25°C for bentonite in deionized water and bentonite in salt water to study the linear viscoelastic range (LVER). The value of strain in LVER was further used in frequency sweep measurements to determine the storage and loss modulus by imposing logarithmic angular frequency sweep from 0.1 ($rad.s^{-1}$) to 100 ($rad.s^{-1}$). Gel strengths of bentonite dispersions were measured in deionized water and salt water (with various electrolyte concentrations) at 25°C using standard API recommended procedure. Before measuring 10-second gel strength, a high pre-shearing at 510 s^{-1} was applied and followed by the 10 seconds hold. Similarly, 10 minutes hold was applied to the bentonite dispersions before measuring 10-minutes gel strength. Very low shear rate 5.1 s^{-1} was applied for measuring gel 10-seconds and 10-minutes strengths as per recommended by API procedure.

3.2.2 Rheological properties using FANN viscometer

Various drilling fluid additives are employed to formulate drilling fluid formulations. Among all the materials used, barite is known as weighting material to control the density of drilling fluid formulations. Drilling fluid density is very important parameter that maintain the column pressure in drilling well during drilling operations and prevent the formation liquid to get into the wellbore. Therefore, a constant amount of barite is used in all the formulation to increase the density of drilling fluids. The rheological properties of drilling fluids such as apparent viscosity, plastic viscosity, gel

strength and yield point are calculated using Fann viscometer model 35. The viscometer consists of bob and rotor sleeve cylindrical geometry and has ability to produce a range of revolution per minutes (rpm). The drilling fluid is placed in the container and dial reading were measured at different rpm values. The mechanism of measuring torque involves the rotation of outer cylinder (rotor sleeve) and shear force on the drilling fluid present in the annular space (between rotor sleeve and bob) transmits the shear force to the rotation of inner bob. The transmitted torque will produce the dial reading at specific rpm value. The rheological properties were calculated by using the standard equation given below:

$$Apparent\ viscosity\ (\mu_p)\ = \frac{\phi_{600}}{2}(cp) \tag{5}$$

$$plastic\ viscosity\ (\mu_p) = \ \phi_{600} - \ \phi_{300}\ (cp) \tag{6}$$

$$Yield\ point\ (Y_{p)} = \ \phi_{300} - \ \mu_p\ (\frac{lb}{100ft^2}) \tag{7}$$

$$Shear\ stress\ (\tau) = 1.065 * \ \phi\ (\frac{lb}{100ft^2}) \tag{8}$$

$$Shear\ rate\ (\dot{\gamma}) = 1.702 * \ \omega \tag{9}$$

Where (ω) is rotor speed measured in rpm and ($\emptyset$) is the dial reading measured in $\left(\frac{lb}{100ft^2}\right)$. Gel strength is also measured using API standard such as 10-sec and 10-min gel strengths. To measure 10-sec gel strength, the drilling fluid in viscometer was left undisturbed for 10 seconds and maximum deflection of dial reading was measure at 3 rpm. Similarly, for measuring 10-min gel strength, the drilling fluid in the viscometer was left undisturbed for 10 minutes and maximum deflection of dial reading was measured by applying 3 rpm. All the rheological properties measured using above mentioned equation in presented in graphical form in results and discussion.

3.2.3 Thermal stability of drilling fluids

Thermal stability of all the formulations was determined after aging in the static oven for 16 hours at 90°C. The filtration and rheological properties of all bentonite/polymer dispersions were measured using API standards.

3.2.4 Filtration properties of drilling fluids

The standard filtration experiments were performed for all bentonite/polymer dispersions based on API recommendation using Fann filter press apparatus. All the filtration experiments were carried out at 25°C before and after aging at 90°C for 16 hours to measure the fluid loss volume. The Whatman filter paper having 25-30 μm pore size was placed at the bottom of filter cell. The filter cell was filled with 300 ml of each sample and tightened into the assembly with T-screw. The pressure of 100 psi was applied as pressing medium. Each experiment was carried out for 30 minutes and total fluid loss volume was measured.

3.2.5 Filter cake permeability analysis

The most preferred properties of water based drilling fluid during drilling operations involves minimum filtrate loss, thin, impermeable and dense filter cake which prevent the invasion of drilling fluid to seep into the formation of wellbore, prevent the wellbore form collapse, prevent the pipe sticking and help in smooth drilling operations. To measure the effectiveness of drilling fluid, determination of permeability filter cake formed on the walls of the wellbore could help us to understand the efficiency and effectiveness of drilling fluid. of One of the important technique to measure the permeability of filter cakes using Darcy's law in which the basis is the flow of liquid through the filter cake. The filtrate volume and square root of time for filtration process has the linear relationship and this relationship is presented by Darcy's law:

$$\frac{dV_f}{dt} = \frac{kA\Delta P}{\mu h_c} \qquad (10)$$

Where V_f is filtrate volume (cm3), t is the time for filtration (sec), ΔP is the pressure drop across the filter cake (Pa), A is the area of filter medium (cm2), μ is the viscosity of filtrate (Pa.s), h_c is the thickness of filter cake (cm) and k is the permeability of filter cake usually reported as (μD). To measure the permeability of filter cake, following three parameters would consider as constant such as ΔP is the pressure drop across the filter cake (690 kPa), A is the area of filter medium (45.6 cm^2), and μ is the viscosity of filtrate (8.90 x 10^{-4}Pa.s).

3.2.6 Scanning electron microscope (SEM) analysis

Scanning electron microscope employed to take high resolution images of filter cakes obtained after the filtration experiment. SEM usually involves high energy beam of electrons to generate high resolution two dimensional images of objects. In the present work, JSM-6610LV scanning electron

microscope (SEM) was used with 10 (μm) width of image at (1000 x magnification) to analyze the surface morphology, structure and arrangements of different drilling fluid additives on the filter cakes. Six filter cake images from SEM were taken to study the effect of bentonite, polymers and nanoparticles on surface morphology on the dried filter cakes from six water based drilling fluid formulations.

3.2.7 Thermogravimetric (TGA) analysis

TGA was performed to study the thermal stability of bentonite by SDT Q600 TA Instrument. About 6.5 mg bentonite sample was placed in microbalance with the heating rate of 10°C/min and scanned from 0^{o}C to 800^{o}C in the nitrogen environment.

3.2.8 X-Ray diffraction (XRD)

XRD analysis was performed by D8 DISCOVER instrument usually used for powder and thin film applications. The XRD has Copper tube anode with 30 mA generators current. The reflection peaks were obtained between $2\theta = 2°$ and 70° with relative intensities. The reflection peaks were analyzed to confirm the components of bentonite.

CHAPTER 4

Rheological Properties of bentonite dispersions: Effect of temperature and electrolyte concentration

4.1 Characterization of bentonite

X-ray fluorescence analysis is one of the important techniques for determining the chemical composition and nature of minerals in clay sample. The results showed that the used sample of clay is Ca-bentonite with major component silicon oxide. The concentrations of silicon oxide and other oxides are listed in Table 4.1.

Table 4.1 X-ray fluorescence analysis of Bentonite

Composition	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**Na_2O**	**CaO**	**K_2O**	**MgO**	**P_2O_5**	**TiO_2**
wt.%	59.7	22.35	5.5	2.23	2.55	1.31	2.77	0.55	0.31

Thermogravimetric analysis TGA was performed to study the thermal stability of bentonite by SDT Q600 TA Instrument. About 6.5 mg bentonite sample was placed in microbalance with the heating rate of 10°C/min and scanned from 30°C to 800°C in the nitrogen environment. Thermal stability and mass loss of bentonite sample upon heating were explained by thermal gravimetric analysis. Figure 4.1 shows the percentage of mass loss of bentonite sample at two distinct steps and it was also confirmed by deriv. weight (%) curve of bentonite which distinctly shows two peaks as shown in Figure 4.1. In the first step, approximately 7% mass loss was in the range of 40°C to 110°C and later 5% mass loss was in the range of 500°C to 700°C. The first mass loss was attributed to the removal

of adsorbed water molecules on cations among the interlayer spaces of bentonite. From 500°C to 700°C, the mass loss was due to dihydroxylation of bentonite surface. The mass loss in this range also includes the loss of non-chemically attached oxides of titanium, phosphorus, calcium, and potassium with other impurities such as sulfur and carbon.

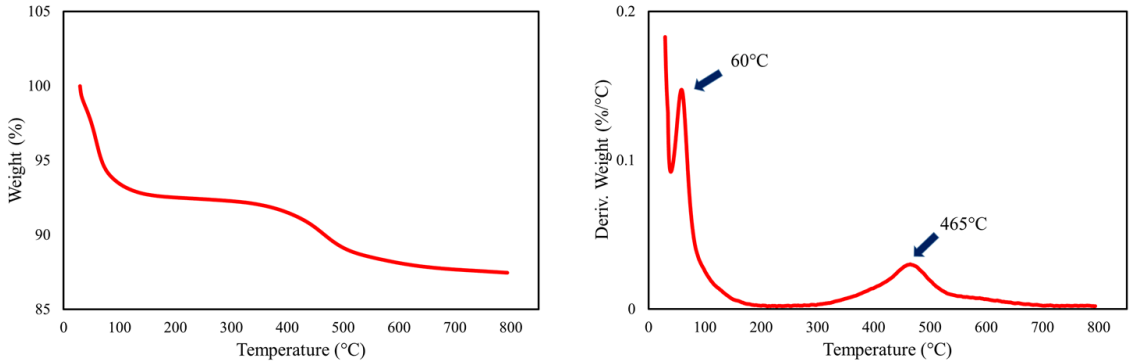

Figure 4.1 TGA of bentonite

The X-ray diffractogram of bentonite sample is presented in Figure 4.2. The investigation of reflection peaks indicates the composition of minerals and their relative height shows the abundance of minerals in the bentonite sample. The reflection peaks occurred at 7.2°, 21.3°, 27°, 50°, 62° and 64° show the presence of quartz. The reflection peaks for feldspar appeared in the range of 24° to 29.5°. Similarly, the major reflection peaks for montmorillonite (Mt) were found at 19°, 35.5°, 39°, 54°, 59° and for calcite reflection peaks appeared in the range of 44° to 48.5°. Both XRD and XRF confirmed that the major component of bentonite is quartz and montmorillonite minerals.

4.2 Effect of bentonite concentration on rheological properties

Rheological behavior of bentonite dispersions was assessed by increasing the concentration of bentonite from 4 m% to 7 m%. Selection of optimum concentration of bentonite is crucial in the drilling industry. Lower concentrations of bentonite may result in poor gel behavior. Conversely, higher concentrations of bentonite will make it highly viscous resulting in the higher power

requirement of the drilling operation. This section deals with rheological properties of bentonite dispersions and rheological parameters obtained by fitting experimental data using four different mathematical models (Cross, Carreau, Bingham, and Herschel-Bulkley) at 25°C.

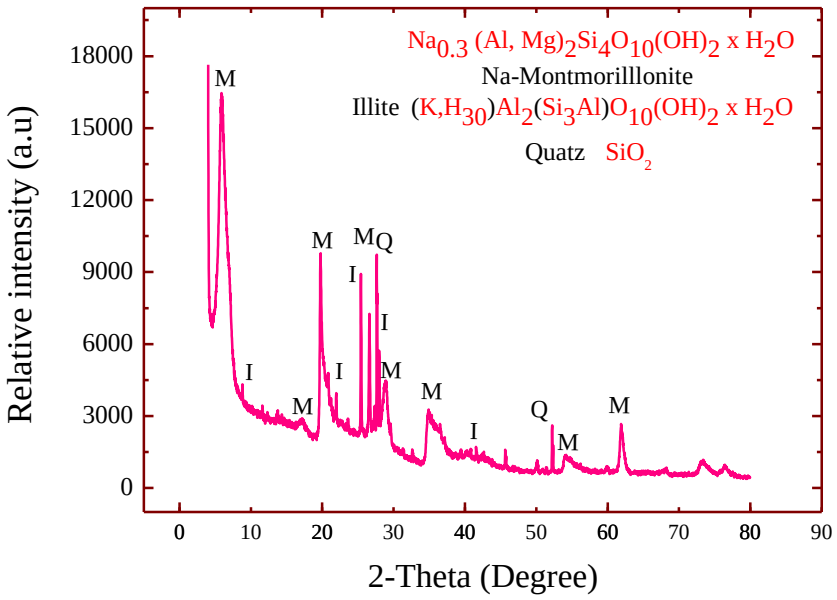

Figure 4.2 XRD spectrum of bentonite

Figure 4.3 represents the effect of bentonite concentration on steady shear viscosity. All the bentonite dispersions indicate shear thinning (pseudoplastic) behavior which means by increasing the shear rate, the viscosity of bentonite dispersion decreases, and similar results were reported in the literature [11, 102]. At low shear rates, a prominent increase in apparent viscosity was observed by increasing bentonite concentration as compared to the high shear rates. This increase in viscosity is due to the interaction among the particles of bentonite. There are two mechanisms which describe the particles

interaction of bentonite in electrolyte free dispersions depending upon the edge to face and edge to edge associations. These associations lead to the formation of card house structure which results in the three-dimensional association of particles interaction and increases the viscosity of bentonite dispersions at higher concentrations.

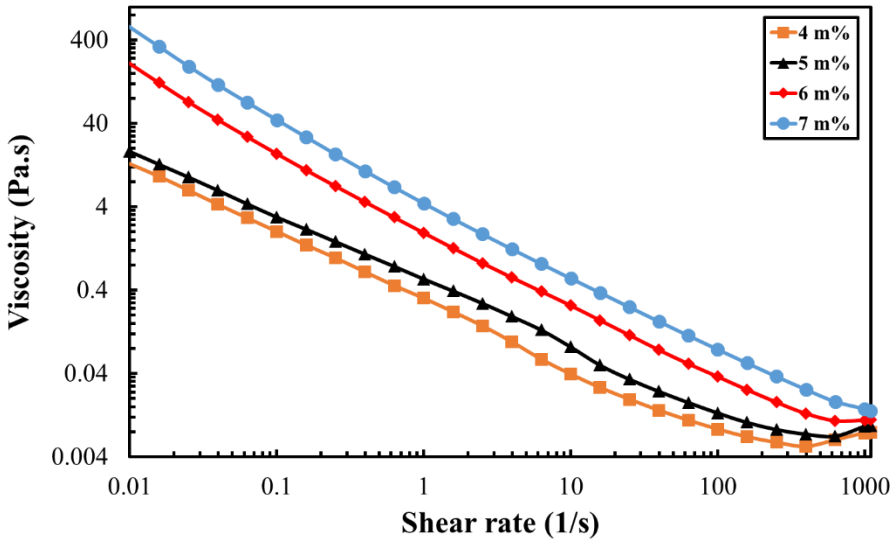

Figure 4.3 Steady shear viscosity of different concentrations of bentonite in deionized water at 25°C

Viscosity vs shear rate data was fitted to Cross and Carreau Models and model parameters are listed in Table 4.2. Results showed that zero shear rate viscosity increases by increasing the concentration of bentonite. This implies that bentonite particles in dispersion have strong inter-particle interactions and these interactions increased by increasing the bentonite concentration. Infinite shear rate viscosity is calculated at very high shear rate approaches to infinity. Low values of infinite shear rate viscosities were observed, which is an indication of the breakdown of inter-particle interactions of bentonite dispersion at high shear rates. Consistency index ‘k’ increased by increasing the concentration of bentonite and this parameter has a great significance for determining the shear thinning properties. Reciprocal of consistency index ‘k’ gives the onset shear rate for shear thinning

at a given concentration. By the increase in bentonite concentration, onset of shear rate for shear thinning moves toward the smaller shear rate. The rate constant ‘m’ of Cross model parameter is a dimensionless parameter which indicates the viscosity dependence on the shear rate in the shear-thinning region and zero value of ‘m’ shows the Newtonian behavior. Increasing value of ‘m’ towards 1 indicates the increase in shear thinning behavior. The value of rate constant increases by increasing the concentration of bentonite, which means shear-thinning behavior increases with concentration.

Table 4.2 Rheological parameters of Cross and Carreau Models at 25°C with different concentration of bentonite

Concentration (m%)	Cross model parameters				Carreau model parameters			
	η_o (Pa.s)	k (s)	m	R^2	η_o (Pa.s)	k (s)	n	R^2
4	48	280	0.91	0.99	31	219	0.12	0.99
5	59.2	260	0.86	0.99	38	201	0.17	0.99
6	2726	2629	0.92	0.99	766	662	0.08	0.99
7	23271	6568	0.99	0.998	2790	759	0.05	0.998

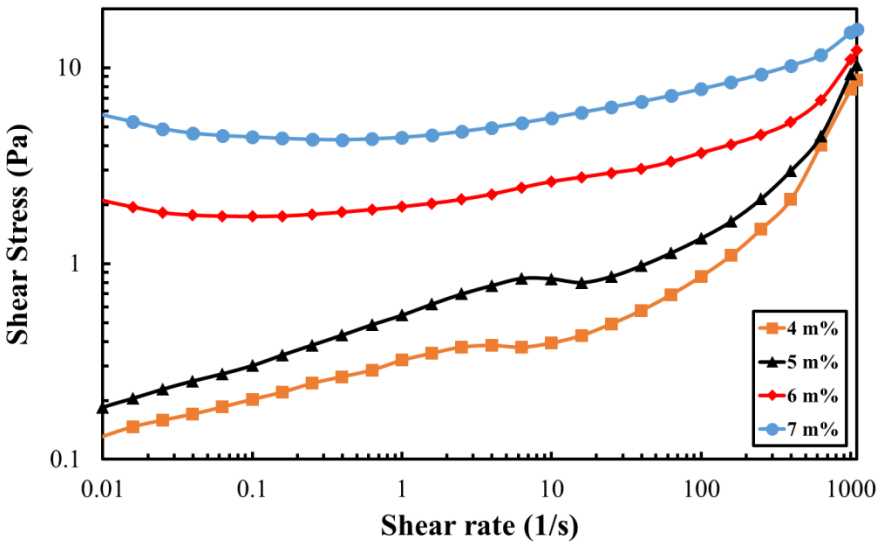

Figure 4.4 The flow curves of bentonite concentrations in deionized water at 25°C

Figure 4.4 represents the effect of four different bentonite concentrations on flow curves at constant temperature 25ºC. At low shear rates, the increase in shear stress was noticed by increasing the bentonite concentration. This increase in shear stress is attributed to the gelation of bentonite particles in the aqueous medium and increased particles associations. A significant increase in shear stress was observed with 6 and 7 m% bentonite concentrations at low shear rates. Shear stress vs shear rate data was fitted to Bingham and Herschel-Bulkley models to study the effect of bentonite concentration on model's parameters that are listed in Table 4.3.

Table 4.3 Rheological parameters of Bingham and Herschel-Bulkley Models at 25°C with different concentration of bentonite

Concentration (m%)	Bingham model parameters			Herschel-Bulkley model parameters			
	τ_o (Pa)	η_p (Pa.s)	R^2	τ_o (Pa)	K ($Pa.s^n$)	n	R^2
4	0.17	7.22e-3	0.98	0.27	6.04e-4	1.36	0.99
5	0.37	8.48e-3	0.97	0.48	1.14e-3	1.29	0.98
6	2.15	8.86e-3	0.97	2.12	0.01	0.94	0.97
7	5.25	0.01	0.89	4.78	0.18	0.58	0.93

Yield stress is the threshold stress that is required to flow the fluid and for drilling fluids yield stress of bentonite dispersions indicates the ability to lift the drilled cuttings to the surface. Bingham yield stress increases 2988% by increasing the concentration of bentonite from 4 m% to 7 m%. Bingham plastic viscosity increases by 38% by increasing the concentration of bentonite. The higher values of correlation coefficient show the best fitting of Herschel-Bulkley model over the wide range of shear rates. Low plastic viscosity indicates the ease of drilling operations while high plastic viscosity makes the drilling fluids highly viscous. A significant increase 1670% in Herschel-Bulkley yield stress was observed with increasing concentration of bentonite from 4 m% to 7 m%. Consistency coefficient 'K' describes the dependence of shear stress on shear rate. The consistency coefficient increases with the increase in bentonite concentration which implies that hole cleaning efficiency

increases. The flow behavior index ‘n’ decreases with the increase in bentonite concentration showing that shear thinning behavior increases.

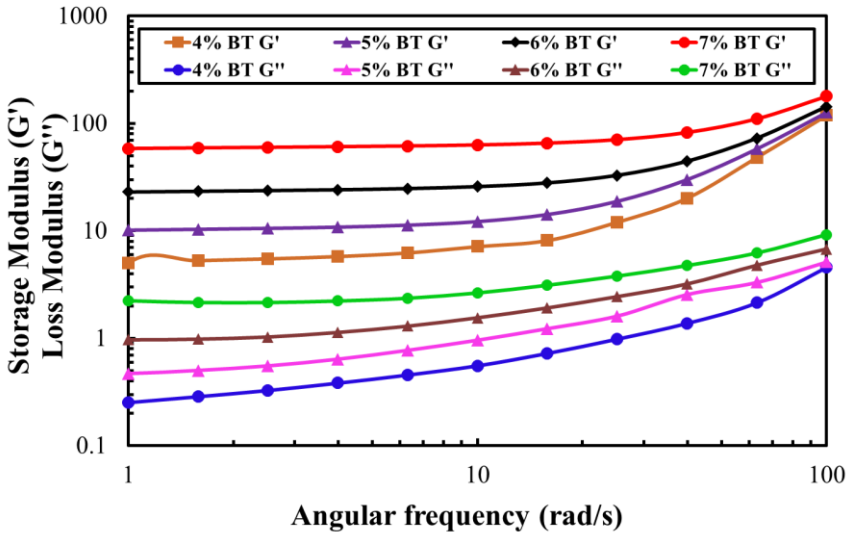

Figure 4.5 Effect of bentonite concentration on storage modulus in deionized water at 25°C

Dynamic rheology test was also performed at 25°C with increasing angular frequency to study the effect of concentration on rheological properties. Storage and loss modulus describes the viscoelastic behavior of bentonite dispersions. Storage modulus describes the energy stored and indicates the elasticity of dispersion and loss modulus describes the energy dissipation as heat and accounts for the viscous portion of bentonite dispersions. The storage and loss modulus increased by increasing the concentration of bentonite as shown in Figure 4.5 which represents that by the increase in bentonite concentration, the structural stability of dispersions increases. The increase of storage and loss modulus results also support the steady shear rheology results which indicate the increase in rheological properties by increasing bentonite concentration. The maximum storage and loss modulus was observed 7 m% of bentonite concentration which indicates that solid like (gel) behavior with high structural stability and high viscous properties respectively. The similar results of storage

and loss modulus were reported in the literature [108]. Gel strength is the ability of bentonite dispersions to suspend the drilled cutting. This property is very important in drilling applications for transporting the drilled cutting to the surface. Figure 4.6 represents the trend of 10-second and 10-minutes gel strengths by increasing concentration of bentonite. 7 m% bentonite dispersions showed the highest value of gel strength due to the excellent gelation behavior of bentonite platelets.

The increase in rheological properties by increasing the concentration of bentonite also attributed to the presence of iron oxide as shown in XRF analysis. The iron oxide particles impart aggregation among the bentonite platelets in the form of three-dimensional network that limits the movement of negatively charged platelets of clay. A three-dimensional network is formed by iron oxide particles that act as bridges among the negatively charges surfaces of bentonite which results in the enhancement of yield stress and viscosity. The overall increase in rheological properties by increasing bentonite concentration is due to the extensive associations among the particles of dispersion.

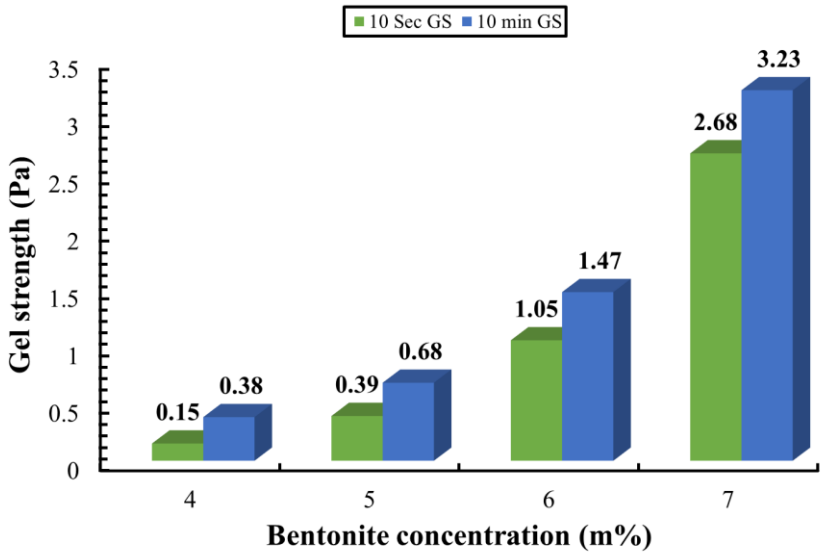

Figure 4.6 Effect of bentonite concentration on gel strength at 25°C

In summary, rheological properties of bentonite dispersions strongly depend on the concentration of bentonite. Yield stress, zero shear viscosity, plastic viscosity, gel strength, and storage modulus increases with increase in concentrations.

4.3 Effect of electrolyte concentration on rheological properties

The interactions of clay platelets greatly affected type and concentration of the electrolytes. This section highlights the results of bentonite dispersions by varying the electrolyte concentration from 0.025 M to 0.1 M NaCl. The effect of electrolyte concentrations on rheological properties was investigated using 5 m% bentonite dispersions and similar results are reported in the literature [29]. The concentration of bentonite lower than 5 m% doesn't give appropriate rheological properties while higher concentration results in the increase in drag and pipe sticking issues in the drilling process.

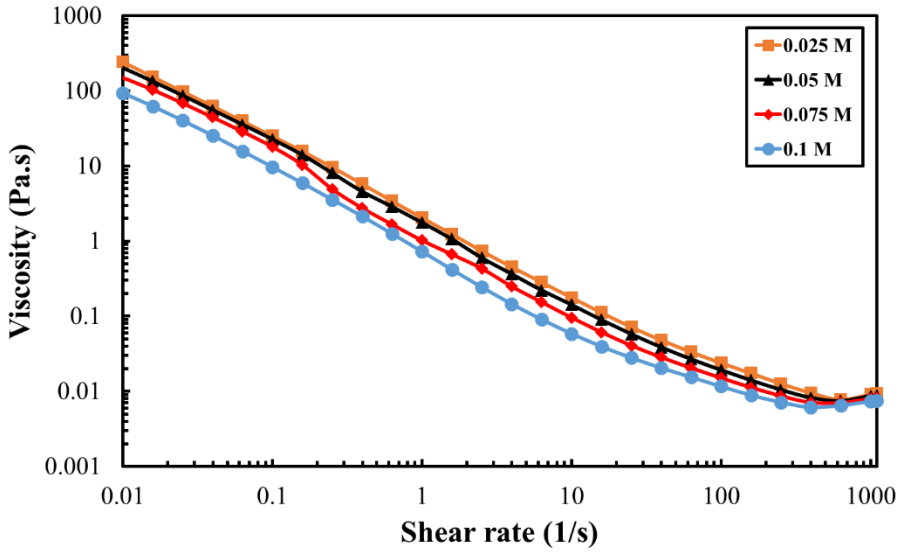

Figure 4.7 Steady shear viscosity profile of 5 m% bentonite in different electrolyte concentrations at 25°C

Figure 4.7 represents the effect of salt concentration on steady shear viscosity. It has been noticed that increasing salt concentration decreases the apparent viscosity of water-bentonite dispersions. The prominent decrease in apparent viscosity is due to the agglomerations of clay platelets by increasing salt concentration. In the presence of an electrolyte, rheological properties are greatly affected by electrostatic interactions and interaction of double layers among the particles of bentonite. The existence of a double layer of cations around negatively charged surfaces of bentonite plays a key role in stabilizing the dispersion by mutual repulsion of the particles. These positively charged ions are attracted towards the negatively charged surface of bentonite due to electrostatic force of attraction. The concentration of counter positive ions is high near to the surface and cations can diffuse away into the lower concentration of the bulk solution. The first layer is known as a stern layer with high concentration of counter positive ions while the second layer is known as a diffuse layer with a lower concentration of ions which can diffuse away from the negatively charged surface in bulk solution.

The concentration of electrolyte will not affect the negative charge on the surface of bentonite particles. It will mainly affect the concentration of counter positive ions in the solution and in the double layer. Increasing the counter ions concentration will compress the double layer and extent of compression will depend on the electrolyte concentration. It means higher the concentration of electrolyte; the extent of double layer compression will be high. At high concentration of sodium chloride (excess number of Na^+ ions), two double layer comes closer to each other through the bridging of sodium ions. The diffuse layer of ions vanishes around the negatively charged surfaces and only one layer of positive ions attracts the two negatively charged surfaces through strong electrostatic force of attraction, thus giving the more compact structure of water-bentonite dispersions. Due to the compression of double layer structure upon adding electrolytes in bentonite

dispersions, rheological properties such as apparent viscosity, plastic viscosity, and yield stress decreases.

Table 4.4 represents the parameters of Cross and Carreau models and their variation with electrolyte concentration. Zero shear viscosity was substantially decreased with the increase in electrolyte concentration, while very small infinite shear rate viscosities was observed for all bentonite dispersion and excluded from the results. The applicability of these models shows the best fitting of experimental data for the whole range of shear rates and in the presence of an electrolyte. The addition of electrolytes enhances face-to-face interactions that result in the increase in flocculation and decreases in viscosity. Consistency coefficient decreases with increasing salt concentration for both models and its reciprocal increases indicate the onset of shear thinning shifts towards the high shear rate by increasing electrolyte concentration. The increase in Cross model parameter 'm' shows that shear thinning behavior of dispersions increases with salt concentration. The decrease in Carreau model parameter 'n' which is also named as power law index reveals that shear thinning property increases with the increase in electrolyte concentration.

Table 4.4 Rheological parameters of Cross and Carreau Models at 5 m% bentonite in different concentrations of electrolyte

Concentration Molarity (NaCl)	Cross model parameters				Carreau model parameters			
	η_o (Pa.s)	k (s)	m	R^2	η_o (Pa.s)	k (s)	n	R^2
0.025	1284	378	1.08	0.99	821	275	0.93	0.99
0.05	657	210	1.11	0.99	479	178	0.91	0.99
0.075	413	170	1.13	0.99	309	148	0.88	0.99
0.1	382	264	1.12	0.99	244	193	0.88	0.99

Figure 4.8 represents the effect of electrolyte concentration on flow curves at 25^{o}C. Shear stress increases with increasing the shear rate and this phenomenon is associated with enhanced interactions among the particles of bentonite. By increasing the electrolyte concentration from 0.025 M to 0.1 M,

shear stress decreases prominently at lower shear rates. A significant decrease in shear stress was observed with a 0.1 M concentration of bentonite dispersion at low shear rate. While at a high shear rate around 1000 $s^{-1,}$ all the flow curves converge at the same point. The decrease in shear stress by increasing electrolyte concentration is attributed to the disruption in network structure and compression of the double layer among the particles of bentonite.

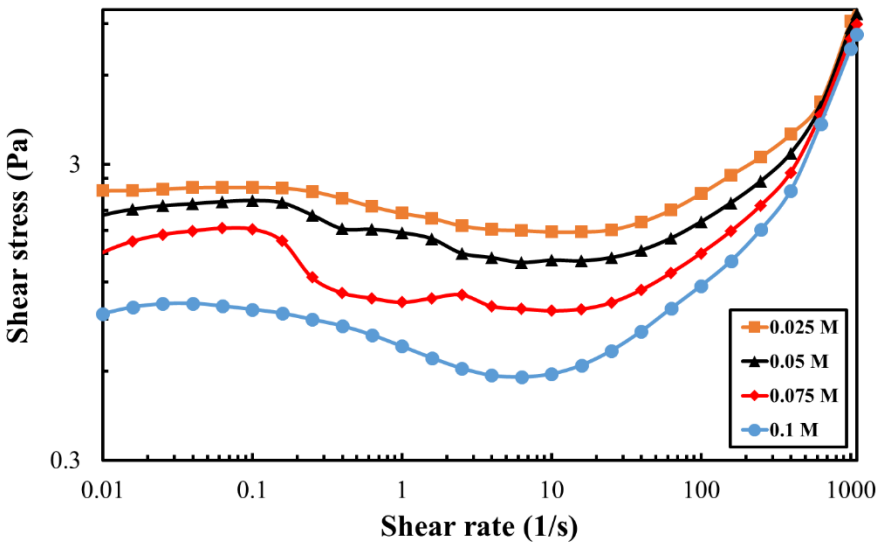

Figure 4.8 Flow curves of 5 m% bentonite in different electrolyte concentrations at 25°C

Table 4.5 shows the parameters of Bingham plastic and Herschel-Bulkley models with various electrolyte concentrations from 0.025 M to 0.1 M NaCl solution at 25°C. The Bingham yield stress and plastic viscosity decreases by increasing electrolyte concentration. A 65% decrease in Bingham yield stress noticed from 0.025 M to 0.1 M concentration and 4.8% decrease in plastic viscosity was observed. While Herschel-Bulkley yield stress decreases 63% with increasing electrolyte concentration. Consistency coefficient 'K' increases with the increase in electrolyte concentration which represents the dependence of shear stress on shear rates and flow behavior index 'n' decreases, which represents the increase of shear thinning behavior with increasing salt concentration. The

decreases in Bingham and Herschel-Bulkley yield stresses are almost same order but the correlation coefficient indicates that Herschel-Bulkley model presents the best fitting of experimental data over the wide range of shear rates from 0.01 s^{-1} to 1000 s^{-1}. Bingham model is only applicable to low shear rates, where shear stress and directly related to shear rate. Above the yield stress, it behaves as a Newtonian model and shows a linear relationship between shear stress and shear rate. But in the actual case, bentonite dispersions in the presence of electrolyte shows non-Newtonian behavior even at high rates and above the yield stress. That's why Herschel-Bulkley model covers the entire range of shear rates and explains well the non-Newtonian behavior of bentonite dispersions.

Table 4.5 Rheological parameters of Bingham and Herschel-Bulkley Models at 5 m% BT in different concentrations of electrolyte at 25°C

Concentration	Bingham model parameters			Herschel-Bulkley model parameters			
Molarity	τ_o (Pa)	η_p (Pa.s)	R^2	τ_o (Pa)	K ($Pa.s^n$)	n	R^2
0.025	1.98	6.71e-3	0.93	2.14	6.70e-5	1.67	0.96
0.05	1.64	6.56e-3	0.92	1.74	4.75e-5	1.65	0.96
0.075	1.11	6.51e-3	0.98	1.23	1.70e-4	1.53	0.97
0.1	0.69	6.38e-3	0.97	0.79	3.50e-4	1.42	0.99

Dynamic rheology test was performed at 25°C to study the effect of electrolyte concentration on rheological properties. Figure 4.9 represents the storage and loss modulus decreases with the increase in electrolyte concentration. A distinctive decrease in storage and loss modulus was noticed at 0.1 M concentration of the electrolyte. This overall decrease in storage and loss modulus represents that elasticity and viscous properties of bentonite dispersions in electrolyte solution decrease which is due to the increase in flocculation in bentonite dispersions. The dynamic rheology results have supported the results of steady shear rheology which indicates that by increasing the concentration of electrolyte in bentonite dispersions, the rheological properties decrease. Figure 4.10 shows a trend of gel strength also affected by increasing electrolyte concentration. Gel strength decreases with increasing electrolyte concentration due to the breakdown of edge to edge and edge to face

interactions and formation of face to face interactions among the bentonite dispersion and lowest gel strength was observed with 0.1 M electrolyte concentration. The overall gelation behavior of bentonite dispersion decreases with the increase of electrolyte concentration.

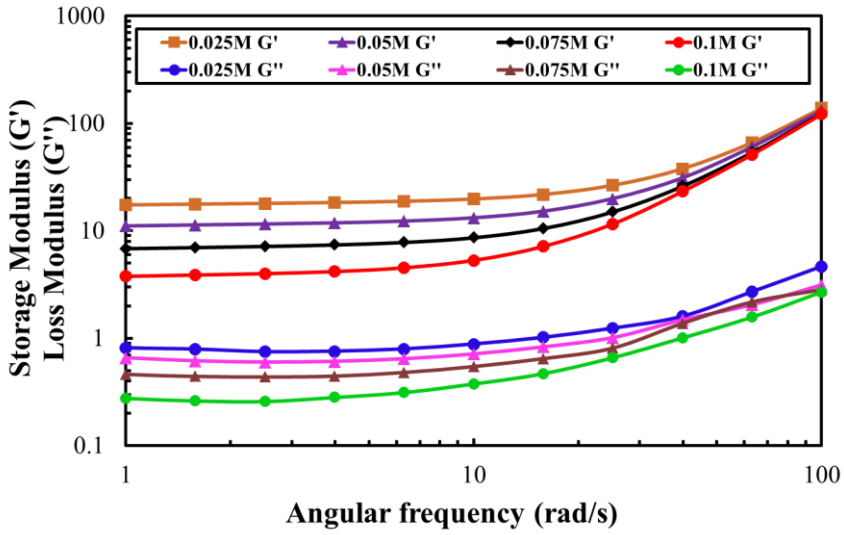

Figure 4.9 Effect of different electrolyte concentrations on storage modulus of 5 m% bentonite dispersions at 25°C

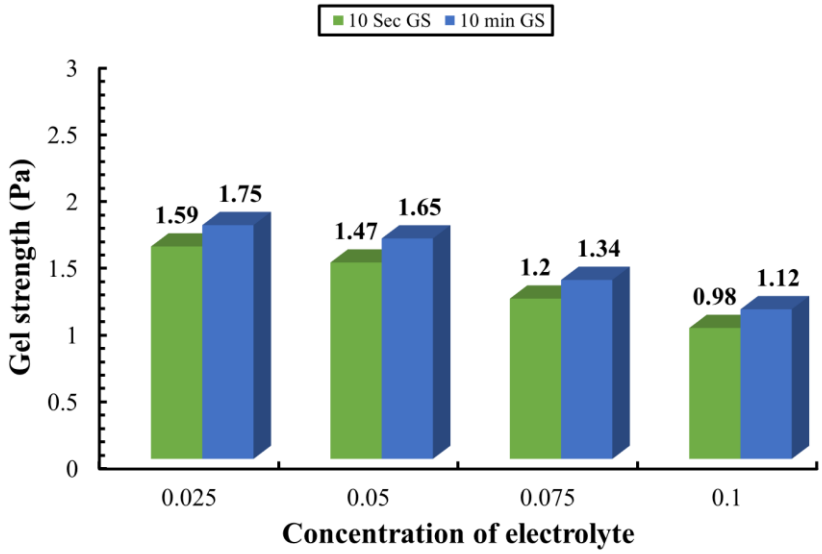

Figure 4.10 Effect of electrolyte concentration of 5 m% bentonite dispersion on gel strength at 25°C

4.4 Effect of temperature on rheology of bentonite dispersions in deionized water

Rheological properties of 5 m% bentonite-water systems were evaluated at four different temperatures. The experimental data were fitted into Bingham and Herschel-Bulkley models to study the effect of temperature on rheological parameters yield stress, apparent viscosity, plastic viscosity and flow behavior index in deionized water.

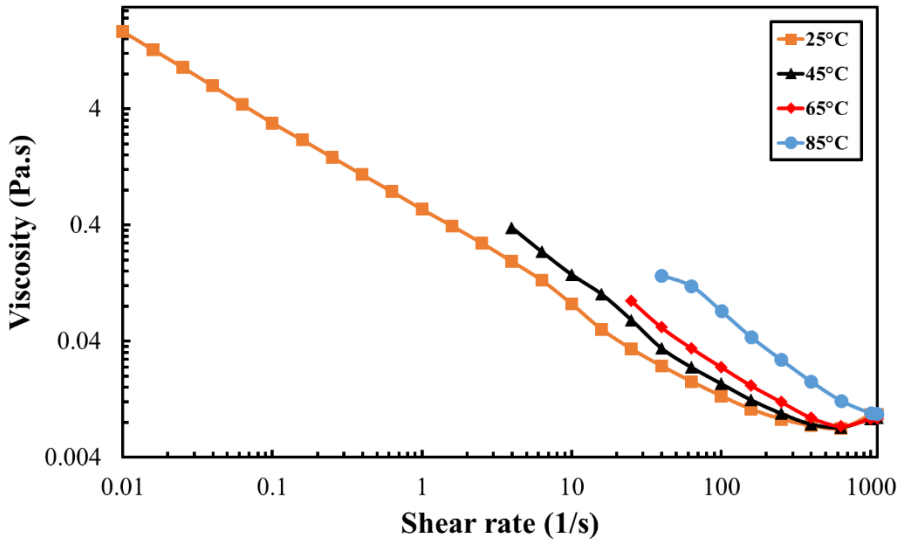

Figure 4.11 Steady shear viscosity profile of 5 m% bentonite dispersion in deionized water at different temperatures

Figure 4.11 represents the steady state viscosity profiles of 5 m% bentonite dispersion in deionized water at four different temperatures. The apparent viscosity of 5 m% bentonite-water dispersion increases by the increases in temperature at a low shear rate 0.01 s^{-1} while at the higher shear rate this change in apparent viscosity was not clearly observed. In fact, all the curves converge nearly at the same point due to the breakdown of interparticle interactions at high shear rates and similar results were reported in the literature for a fixed concentration of bentonite [30]. At a particular temperature, particles of bentonite dispersions are in dispersed state and associated with each other through edge

to face mode of interactions. When temperature increases, the dispersed state particles moved due to Brownian motion and changed into cluster form by making face to face interactions among the platelets of bentonite. Higher temperature may increase the frequency of breakdown of the cluster but there is an equilibrium at which the frequency of cluster formation through face to face interactions is high as compared to the frequency of cluster break down. At higher temperature, face to face interactions are made due to the increased ionic activity in bentonite dispersions. The cations surrounded the clay platelets moved into the solution resulting in the compression of a double layer with increased face to face interactions and cluster formation among the particles. Thus, increase in temperature increases the rheological properties of bentonite dispersions.

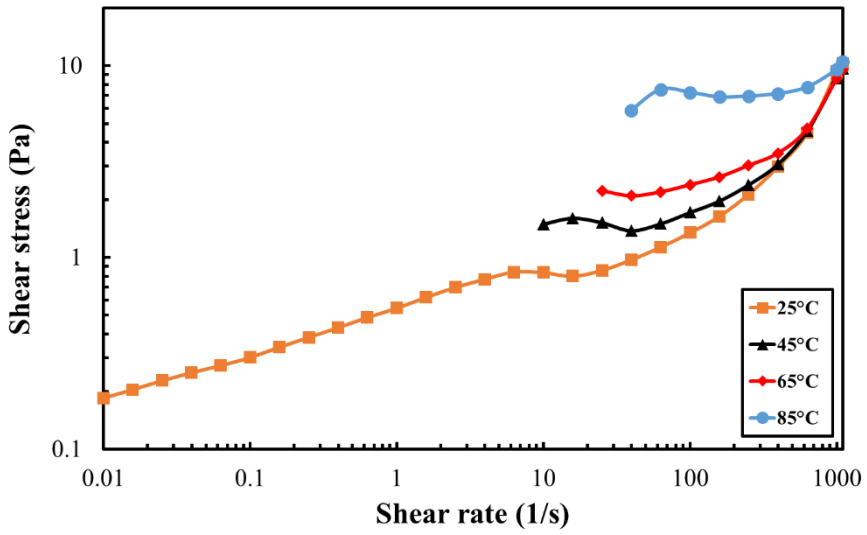

Figure 4.12 Flow curves of 5 m% bentonite dispersion in deionized water at different temperatures

Figure 4.12 represents the flow curves of 5 m% bentonite-water system tested at four different temperatures. At low shear rates, shear stress increases with the increase in temperature but at higher shear rates, all the curves for shear stress converge at the same point.

Bingham plastic and Herschel-Bulkley models were applied to the data to study the rheological behavior of at different temperatures and all the model parameters are reported in Table 4.6 . The

Bingham yield stress increases 625% with the increase in temperature while Bingham plastic viscosity decreases 5.7% with the increase in temperature from 25°C to 85°C. The Herschel-Bulkley yield stress increases 258% with the increases in temperature from 25°C to 85°C. the increase of yield stress with the rise in temperature is due to the thermal induce swelling and flocculation of bentonite platelets.

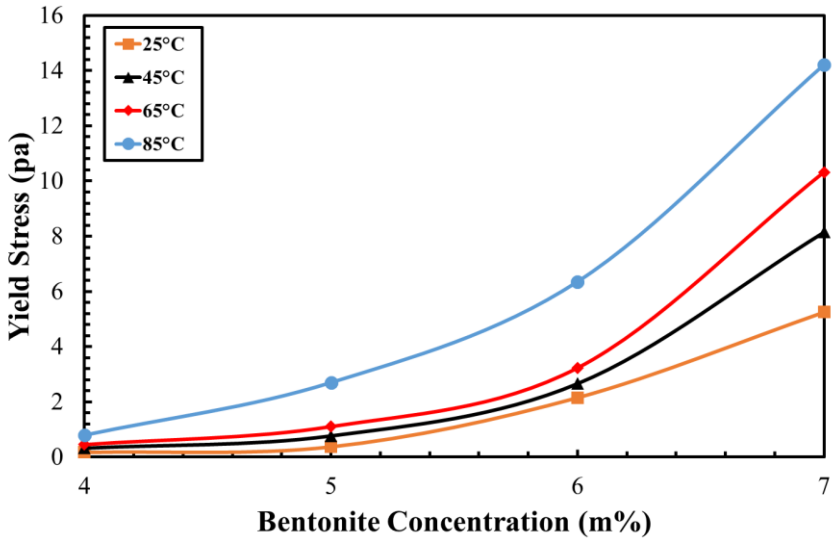

Figure 4.13 Effect of bentonite concentration on Bingham yield stress at different temperatures

The correlation coefficient shows that Herschel-Bulkley model is the best fitting of experimental data. Although for Bingham model correlation coefficient decreases abruptly with the increase in temperature which shows that Bingham model is not applicable for the high temperature at high shear rates. The consistency coefficient 'K' indicates the relationship with viscosity and increase in temperature increases the steady shear viscosity at a given shear rate. For temperature 25°C and 45°C, the flow behavior index 'n' is higher than unity indicating the shear thickening behavior of bentonite dispersions. The decreasing trend of flow behavior index 'n' with the rise in temperature at 65°C and 85°C illustrates the shear thinning behavior of bentonite dispersions. The increase in

temperature of bentonite-water dispersions displays non-Newtonian behavior at a higher temperature and a similar trend of rheological parameters was reported in the literature [31].

Table 4.6 Rheological parameters of Bingham and Herschel-Bulkley Models with 5 m% bentonite at different temperatures

Temp °C	Bingham model parameters			Herschel-Bulkley model parameters			
	τ_o (Pa)	η_p (Pa.s)	R^2	τ_o (Pa)	K (Pa. s^n)	n	R^2
25	0.37	8.48e-3	0.97	0.48	1.14e-3	1.29	0.98
45	0.76	7.56e-3	0.96	0.84	1.75e-3	1.21	0.96
65	1.10	7.30e-3	0.91	1.04	0.02	0.86	0.91
85	2.69	7.99e-3	o.65	1.72	0.60	0.37	0.82

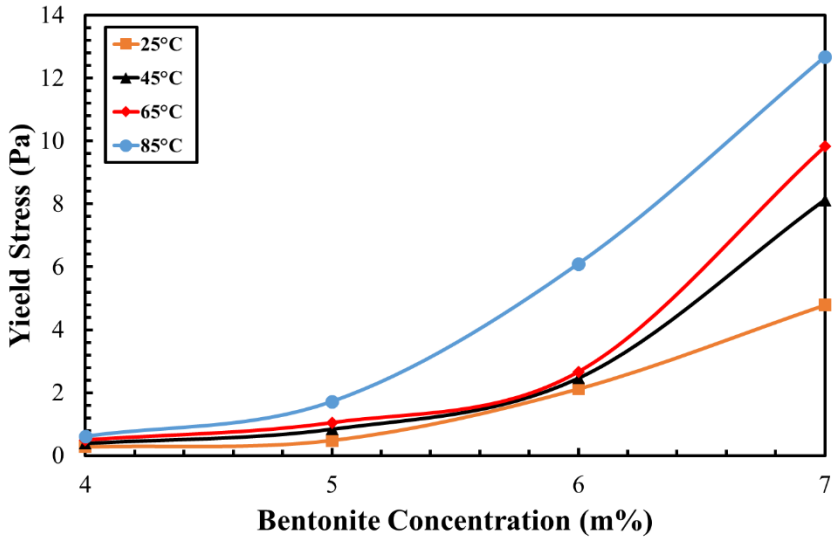

Figure 4.14 Effect of bentonite concentration on Herschel-Bulkley yield stress at different temperature

Figure 4.13 and Figure 4.14represents the variation of Bingham and Herschel-Bulkley yield stress with bentonite concentration at various temperatures from 25°C to 85°C in deionized water. By increasing the concentration of bentonite, yield stress increases exponentially due to the enhanced interactions among the particles of bentonite. For a given concentration, Bingham and Herschel-Bulkley yield stress increased by increasing the temperature and prominent increase in the yield stress was noticed at 85°C with 7 m% bentonite concentration.

4.5 Effect of temperature on rheology of bentonite dispersions in salt water

This section explains the rheological properties of 5 m% bentonite dispersion in the presence of fixed electrolyte concentration at four different temperatures. Rheological properties were determined by fitting shear stress vs shear rate data into Bingham and Herschel-Bulkley models. The effect of temperature on yield stress, apparent viscosity, plastic viscosity and flow behavior index was discussed.

Figure 4.15 represents the steady shear viscosity profiles of bentonite dispersions in 0.025 M salt water at different temperatures. The viscosity of bentonite dispersion in salt water increases with the increase in temperature. The increase of viscosity is prominent at low shear rates due to the existence of structural bonds among the particles. While at high shear rates, all the steady shear viscosity profile decreases and converged around the single point due to the rupture of bonds among particles. The higher temperature increases the steady shear rate viscosity due to the combined effect of cluster formation and compression of a double layer with the increase in temperature.

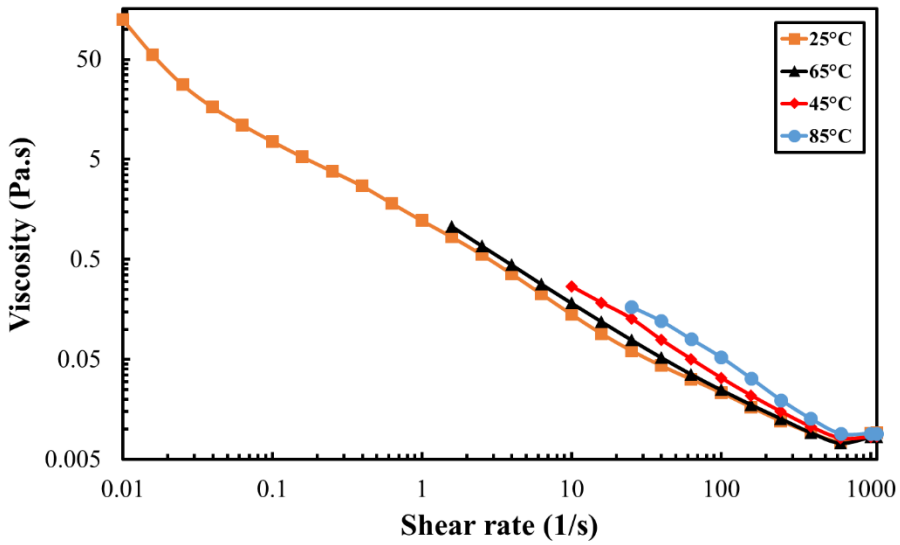

Figure 4.15 Steady shear viscosity profile of 5 m% bentonite concentration in (0.025 M) salt water at different temperatures

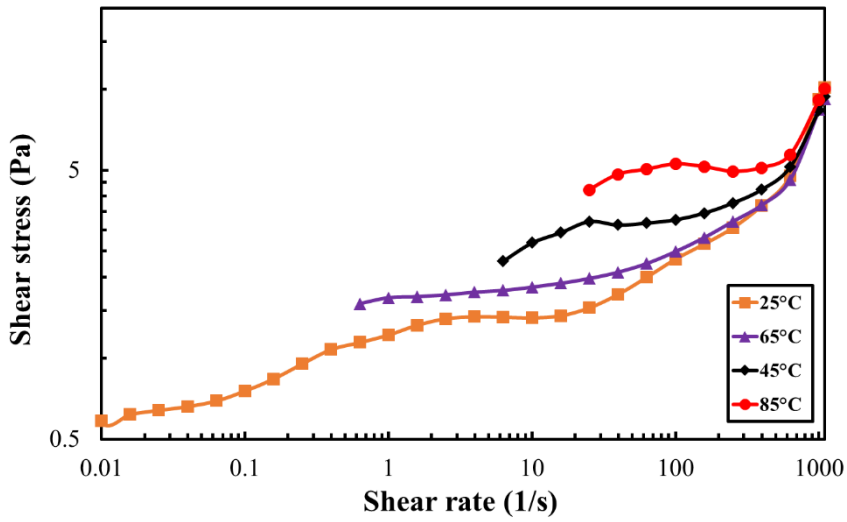

Figure 4.16 The flow curves of 5 m% bentonite concentration in (0.025 M) salt water at different temperatures

Figure 4.16 represents the effect of different temperatures on flow curves of 5 m% bentonite in the presence of 0.025 M sodium chloride solution. It indicates the increasing trend of shear stress by increasing shear rate from 0.01 s^{-1} to 1000 s^{-1}. At low shear rates, this change in shear stress at a different temperature is high but at the high shear rate, this change in shear stress is not prominent. Bingham plastic and Herschel-Bulkley models were applied to the shear stress vs shear rate data to study the rheological behavior of bentonite dispersions in the presence of electrolyte at different temperatures and all the model parameters are listed in Table 4.7. Bingham yield stress increases 1478% with an increase in temperature while plastic viscosity decreases 19% with temperature increase from 25°C to 85°C. Herschel-Bulkley yield stress increases 142% with the rise in temperature up to 85°C due to the thermal induce swelling of bentonite platelets which results in the flocculation among the platelets. Flow behavior index 'n' of Herschel-Bulkley model shows the increase up to 65°C which represents the shear thickening behavior. At 85°C, the value of flow

behavior index ‘n’ decreases from one, which shows shear thinning behavior at elevated temperature. The correlation coefficients show the best fitting of experimental data in Herschel-Bulkley models over the entire range of shear rates.

Table 4.7 Rheological parameters of Bingham and Herschel-Bulkley Models with 5 m% bentonite in 0.025 M NaCl electrolyte at different temperatures

Temp °C	Bingham model parameters			Herschel-Bulkley model parameters			
	τ_o (Pa)	η_p (Pa.s)	R^2	τ_o (Pa)	K (Pa. s^n)	n	R^2
25	1.98	6.71e-3	0.93	2.14	6.70e-6	1.67	0.96
45	2.32	5.64e-3	0.91	2.44	8.29e-6	1.61	0.94
65	3.05	5.20e-3	0.54	3.15	1.24e-5	1.48	0.55
85	4.56	4.99e-3	0.51	4.86	3.38e-5	1.39	0.54

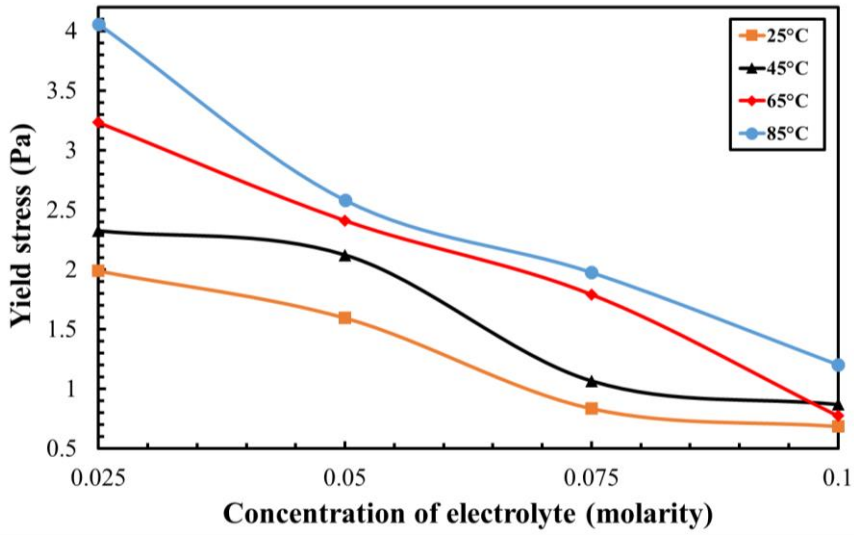

Figure 4.17 Effect of electrolyte concentration of 5 m% bentonite dispersion on Bingham yield stress at different temperatures

Figure 4.17 and Figure 4.18 represents the variation of Bingham and Herschel-Bulkley yield stress of 5 m% bentonite dispersions respectively with the variation of electrolyte concentration at various temperatures from 25°C to 85°C. By increasing the concentration of electrolyte at given temperature, Bingham yield stress and Herschel-Bulkley yield stress decreases due to the suppression of double layer which results in agglomeration. At a given concentration, Bingham and Herschel-Bulkley yield

stress increased by increasing the temperature. The prominent increase in yield stress was noticed at 85°C with 0.025 M concentration of electrolyte.

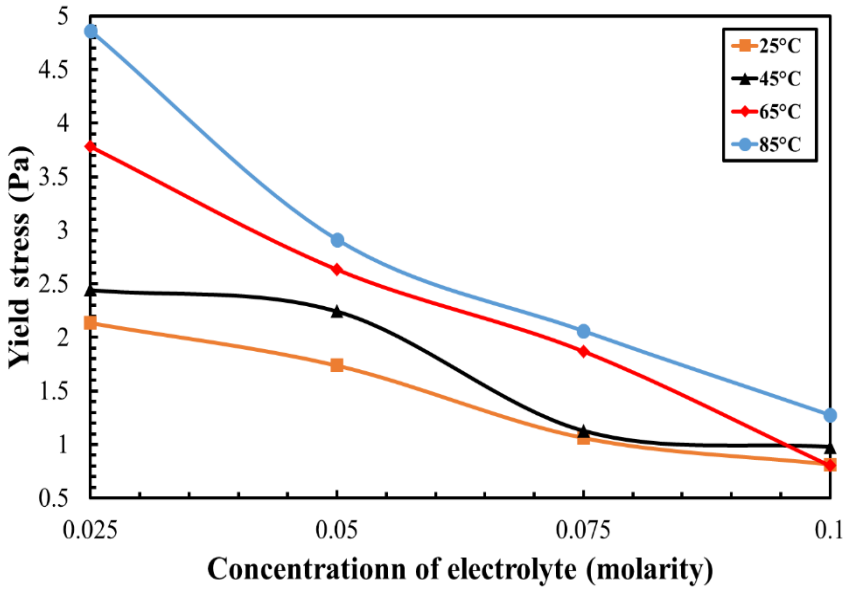

Figure 4.18 Effect of electrolyte concentration of 5 m% bentonite dispersion on Herschel-Bulkley yield stress at different temperatures

CHAPTER 5

High molecular weight copolymers as rheology modifiers and fluid loss additives for water based drilling fluids

The discussion of this chapter is divided into four different sections. The first section deals with the rheological properties of three water-soluble acrylamide-based copolymers without bentonite. The second section describes the rheological properties of bentonite/polymer dispersions. Third and fourth sections discuss the thermal stability and filtration properties of bentonite/polymer dispersions, respectively.

5.1 Rheological properties of polymer solutions

Figure 5.1 represents the steady shear viscosity of polymer solutions (without bentonite) as a function of shear rate at 25°C. All the polymer solutions show shear thinning behavior. The steady shear viscosity of polymer solution differs based on functional group distribution, ionic strength, DOH, polymer molecular weight, conformations of polymer chains, and surface charge. In this study, the effect of DOH and nature of polymer chains are mainly discussed. The polymer solution P3 shows minimum shear viscosity as compared to P1 and P2 polymer solutions due to the presence of small of acrylate side group. The DOH of P3 polymer is intermediate to that of P1 and P2. The P1 and P2 polymer solutions have same comonomer (2-Acrylamido-2-Methylpropane Sulfonic Acid) but differ in DOH. The polymer that has a higher DOH contains a substantial number of functional groups with replaceable metal ions. Due to the higher DOH of P2 polymer solution shows high shear viscosity compared to the P1 polymer solution.

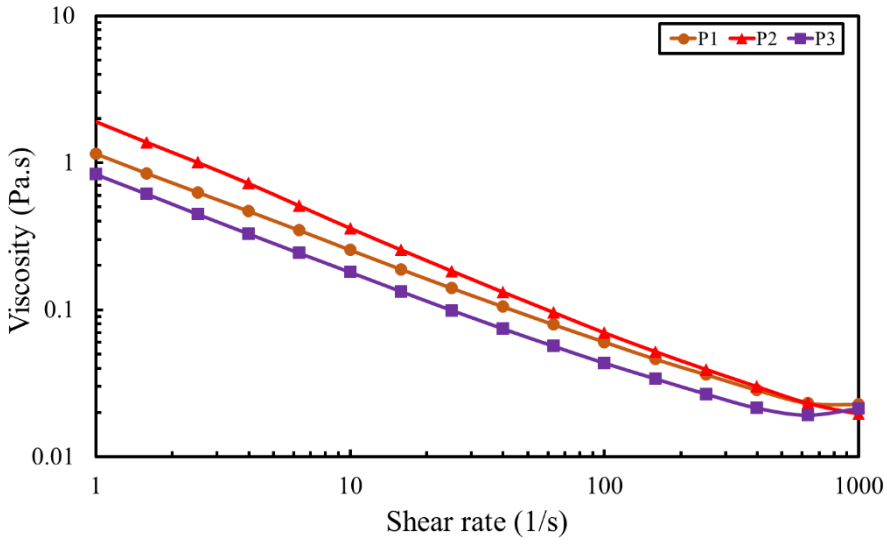

Figure 5.1 Steady shear viscosity of different polymers at 25°C in deionized water

The flow curves of polymer solutions at 25°C are represented in Figure 5.2. Polymer solution P3 has lowest shear stress while P2 has highest shear stress at 1 s^{-1} shear rate. The P1 polymer solution has 38% high yield stress compared to the P3 polymer solution while P2 polymer solution has 65% high yield stress compared to the P1 polymer solution at 1 s^{-1} shear rate. The change in shear stress at the low shear rate is more prominent because of strong interactions between the polymer chains. While at high shear rates, the polymer chains align in the direction of flow and change in shear stress was not prominent. In summary, the rheological results of polymer solutions (without bentonite) suggest that the acrylamide-based copolymers containing acrylic acid have higher viscosity compared to the copolymer having AMPS as a comonomer. In addition, the acrylamide-AMPS copolymer having a higher DOH exhibited a higher viscosity. After evaluating the rheological properties of polymers, we were further interested to see how these polymers interact with bentonite. Therefore, detailed rheological investigation of bentonite/polymer dispersion was conducted.

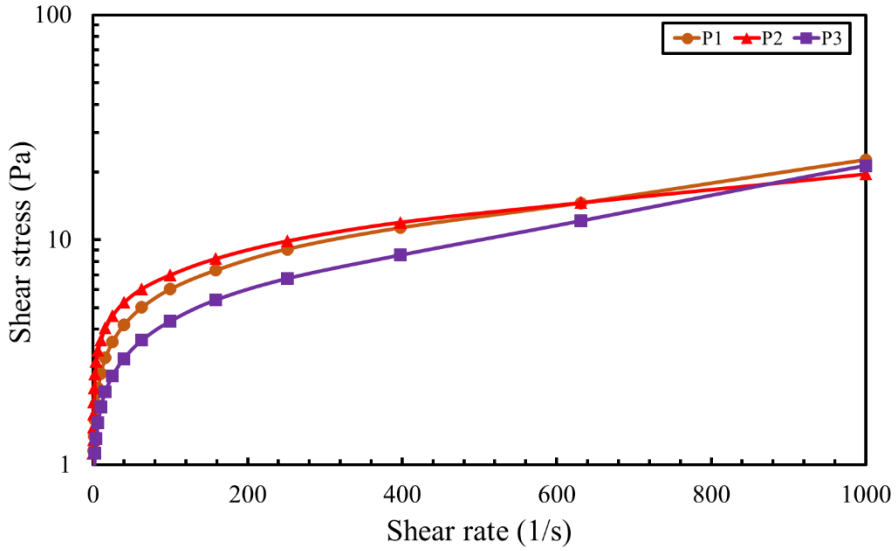

Figure 5.2 Flow curves of different polymers at 25°C in deionized water

5.2 Rheological properties of bentonite/polymer dispersions

The rheological properties of bentonite/polymer dispersions in deionized water were studied at 25°C and 85°C. Figure 5.3 represents the steady shear viscosity of bentonite and bentonite/polymer dispersions at 25°C. All added polymer enhanced the rheological properties of bentonite. The low steady shear viscosity of bentonite dispersion was attributed to the weak interactions among the platelets of bentonite in deionized water. The interactions of bentonite with polymer molecules could be explained in two different ways. The first is adsorption of polymer chains on bentonite platelets and second is ionic interactions due to the presence of negative charges on functional groups on polymer molecules and positively charged edges of bentonite platelets. BT/P3 dispersions showed highest steady shear viscosity due to the greater interactions of acrylate group with positively charged edges of bentonite platelets. These results are interesting and opposite that was observed for aqueous solutions of polymers (without bentonite). The viscosity of the P3 polymer was lowest compared to other polymers (Figure 5.1). However, in bentonite/polymer dispersions, the bentonite/P3 polymer

dispersion showed maximum viscosity compared to other bentonite/polymer dispersions. This is because small acrylate group offers less hindrance compared to bulky groups and attach with bentonite at multiple points and interacts with positively charged edges of bentonite and it creates strong ionic interaction which leads to the improved rheological properties of BT/P3 polymer dispersion. BT/P1 and BT/P2 dispersions have less shear viscosity compared to the BT/P3 dispersion. This is attributed to the lesser interactions of the bulky functional group (2-Acrylamido-2-Methylpropane Sulfonic Acid) with bentonite platelets due to the stearic hindrance of the bulky group along the polymer chains. On the other hand, the BT/P2 dispersions have high viscosity compared to the BT/P1 dispersion due to the higher DOH of the P2 polymer. Higher DOH indicated that there are more ionizable functional groups along the polymer chain which can interact with bentonite platelets and gives better rheological properties. In summary, the acrylamide-based copolymers containing smaller comonomers (acrylic acid) showed better rheological properties in bentonite/polymer dispersions compared to the bulky comonomers (AMPS). The degree of hydrolysis of the polymers is another important factor and rheological properties of bentonite/polymer dispersions depend on DOH of the polymer as well.

The steady shear viscosities of bentonite and bentonite/polymer dispersions at 85°C are represented in Figure 5.4. All the viscosity curves of bentonite and bentonite/polymer dispersions represent pseudo-plastic behavior that indicates the decrease in the viscosity by increasing the shear rate and similar results are reported in the literature [49]. The increase in the temperature of bentonite dispersion increases the steady shear viscosity due to the flocculation and thermal induce swelling of bentonite platelets. Similarly, elevating the temperature of bentonite/polymer dispersions to 85°C results in the increase in steady shear viscosity compared to the bentonite/polymer dispersions at 25°C. As the shear rate increases, the viscosity of bentonite/polymer dispersion decreases. Similar

to low-temperature behavior, the BT/P3 dispersion shows the highest viscosity compared to the BT/P1 and BT/P2 dispersions at 85 °C as well. This indicates that acrylamide-based copolymers with smaller comonomer show better rheology at low and high temperatures in bentonite/polymer dispersions compared to the copolymers containing bulky comonomers.

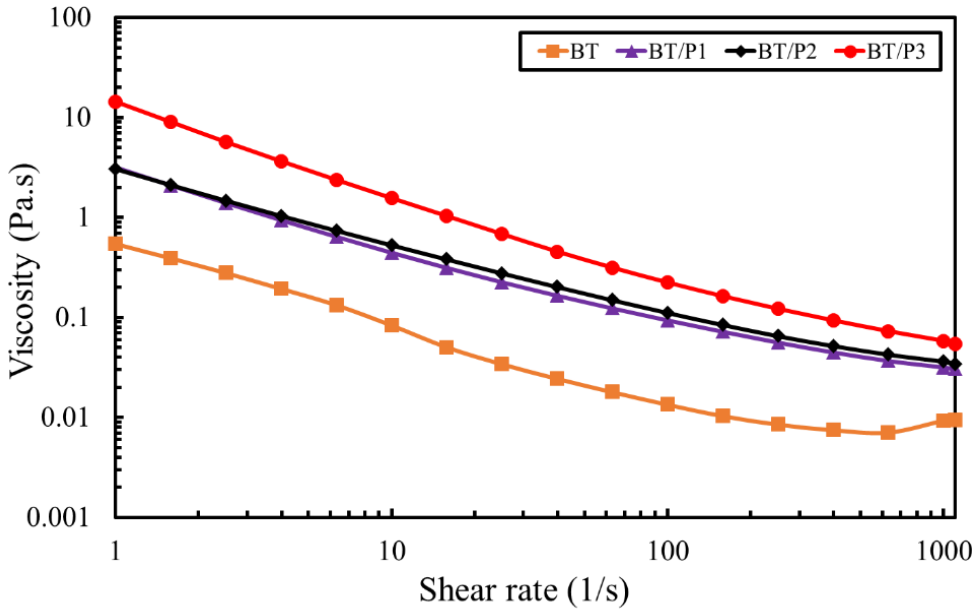

Figure 5.3 Steady shear viscosity of bentonite and bentonite/polymer suspensions at 25°C in deionized water

The flow curves of bentonite and bentonite/polymer dispersions are represented in Figure 5.5 and Figure 5.6 at 25°C and 85°C, respectively. All the flow curves of bentonite and bentonite/polymer dispersions exhibit non-Newtonian shear thinning behavior at 25°C and 85°C. The shear stress vs shear rate data was fitted to Herschel-Bulkley model at 25°C and 85°C and the rheological parameters are listed in Table 5.1. At low shear rate and 25°C, the shear stress of bentonite dispersion has the lowest value compared to bentonite/polymer dispersions. BT/P3 dispersion showed the highest value of shear stress compared to all other dispersions. The order of increment in shear stress was given as BT<BT/P1< BT/P2< BT/P3. The shear stress values at 85°C followed the same trend

but with slightly higher values. The yield stress values showed that BT/P1 dispersion has the minimum, while BT/P3 dispersion has the maximum value of yield stress at 25°C. The yield stress values increases for all dispersions at 85°C due to the enhanced flocculation of bentonite in bentonite/polymer dispersions. The higher value of yield stress is needed in drilling fluid operations for cutting transport to the surface.

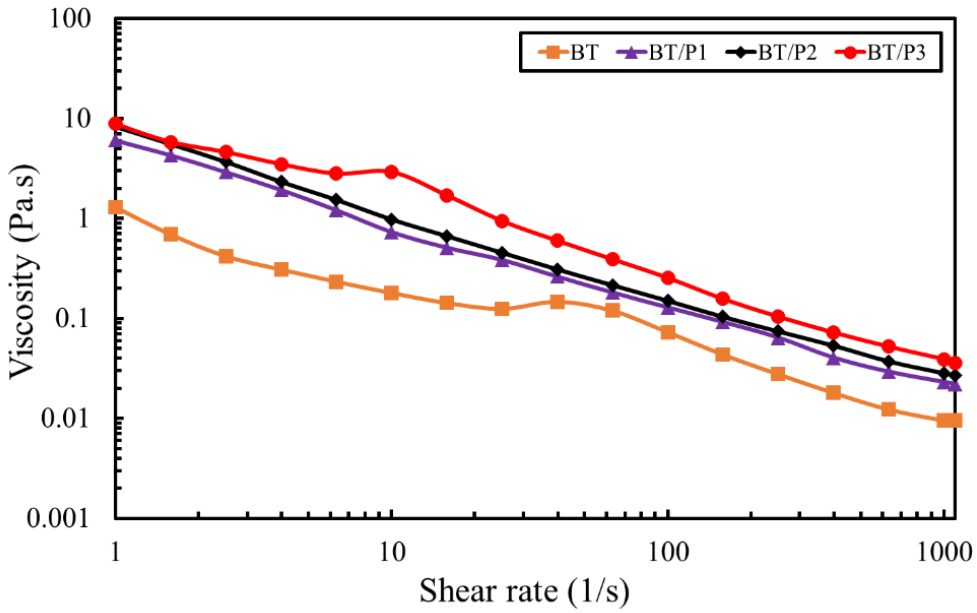

Figure 5.4 Steady shear viscosity of bentonite and bentonite/polymer suspensions at 85°C in deionized water

The rheological parameters extracted using Herschel-Bulkley model for bentonite and bentonite/polymer dispersions at 25°C and 85°C are listed in Table 5.1. Consistency coefficient 'K' represents the dependence of shear stress on shear rate, interactions of drilling fluid components with each other and the hole cleaning efficiency. The increase in consistency coefficient was observed from 25°C to 85°C for all the formulations. But at 85°C, the consistency coefficient 'K' has higher values compared to the values at 25°C which depict that at higher temperature the shear stress is

more dependent on shear rate and better hole cleaning efficiency. The value of flow behavior index 'n' represents that all the formulations have shear thinning (pseudo-plastic) behavior. The flow behavior index at two temperatures 25°C and 85°C are listed in Table 5.1. The comparison of 'n' values shows that at elevated temperature bentonite and bentonite/polymer dispersions indicates the significant shear thinning (pseudo-plastic) behavior.

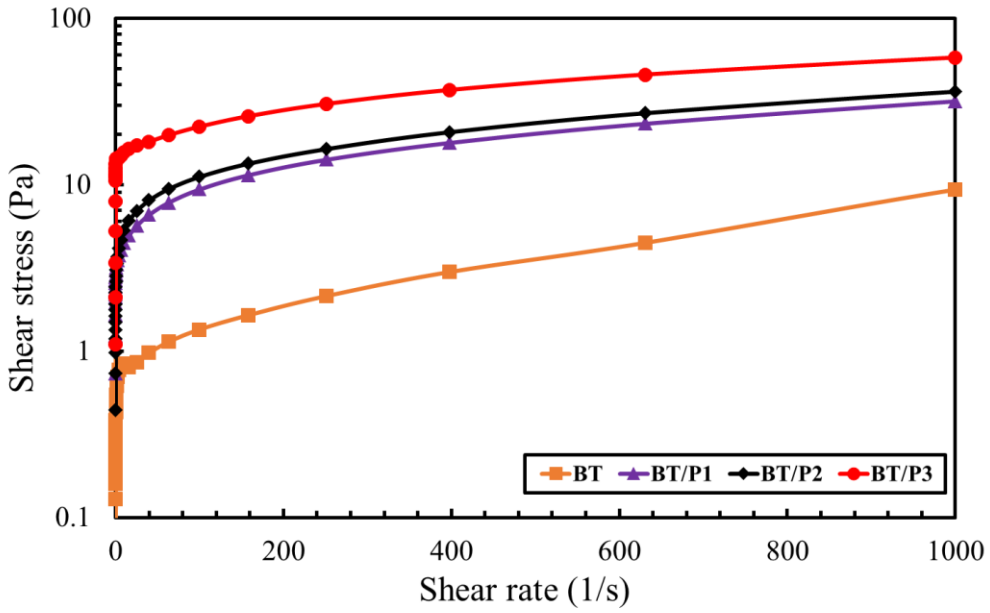

Figure 5.5 Flow curves of bentonite and bentonite/polymer dispersions at 25°C in deionized water

Gel strength is one of the key property of drilling fluids which shows the ability of solid suspension during the drilling process. Gel strength of water-based drilling fluids strongly affected by the solid contents, bacteria, acidic gases, and salts. Temperature also affects the performance of water-based drilling fluids which contain polymers and bentonite as a principle component. The gel strength of bentonite and bentonite/polymer dispersions at 25°C and 85°C are presented in Figure 5.7 and Figure 5.8respectively. The higher gel strength is required in drilling operations to suspend rock cuttings. The order of 10-seconds and 10-minutes gel strength for bentonite and bentonite/polymer dispersion

follow the trend of BT<BT/P1< BT/P2< BT/P3. The higher gel strength of BT/P3 is attributed to the strong interactions of bentonite and P3 polymer due to the presence of acrylate functional group. Acrylate functional group is small and offers less stearic hindrance. The gel strength at 85°C represents a substantial increase in values due to the flocculation of bentonite and bentonite/polymer dispersions.

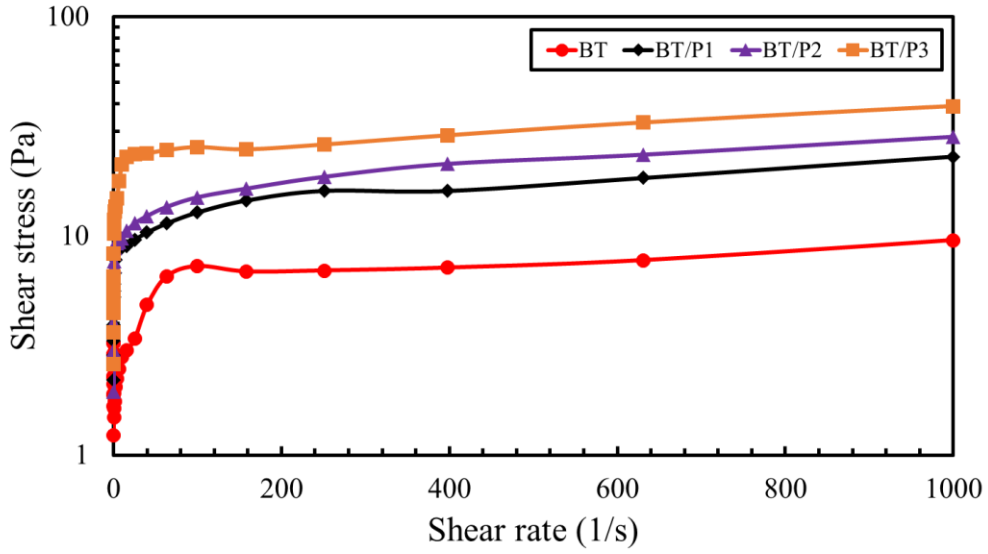

Figure 5.6 Flow curves of bentonite and bentonite/polymer suspensions at 85°C in deionized water

Table 5.1 Rheological parameters of Herschel-Bulkley model at 25°C and 8°5 for different formulations of bentonite and polymers

Formulations	Herschel-Bulkley Model at 25°C			Herschel-Bulkley Model at 85°C		
	Yield stress	Consistency Index "K" (Pa.s^n)	Flow behaviour index "n"	Yield stress	Consistency Index "K" (Pa.s^n)	Flow behaviour index "n"
BT	0.83	2.83e-4	0.48	1.72	1.19	0.38
BT/P1	3.18	0.58	0.68	3.62	3.2	0.29
BT/P2	3.25	0.91	0.63	3.88	3.6	0.29
BT/P3	13.7	1.11	0.69	21.6	1.14	0.34

In summary, rheological properties of bentonite improved significantly using high molecular weight polymers. The addition of polymers in bentonite dispersion enhances the rheological properties such as viscosity, yield stress, and gel strength. The superior rheological properties of the P3 polymer solution in BT/P3 dispersion at 25°C and 85°C makes it a suitable candidate for drilling fluids. These excellent rheological properties of BT/P3 dispersion is due to the strong chemical interactions among the polymer functional groups with positively charged edges of bentonite platelets. It was observed that the increase in DOH of polymer chains would improve the rheological properties of bentonite/polymer dispersions.

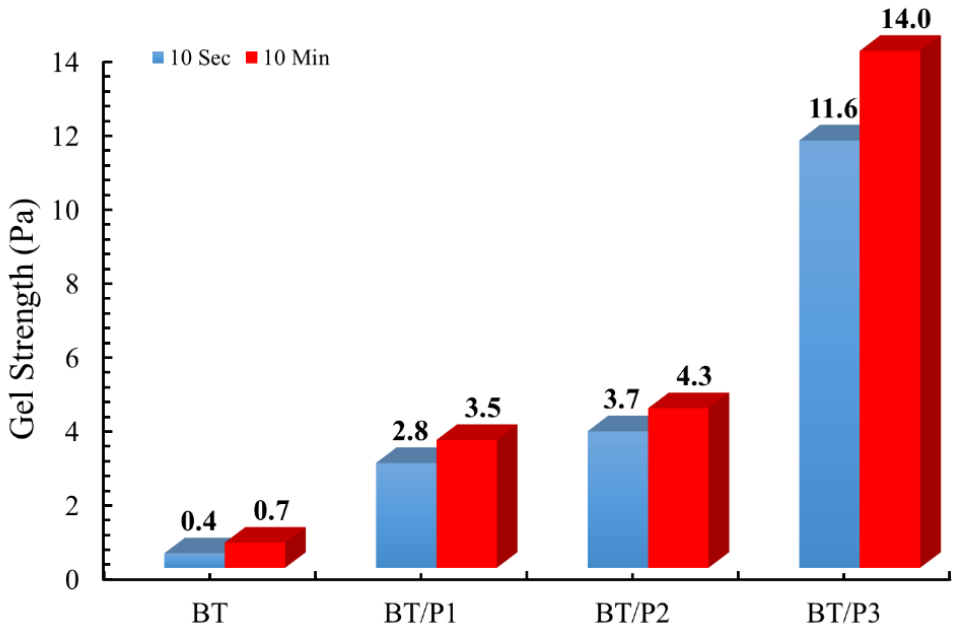

Figure 5.7 Gel strength of bentonite and bentonite/polymer suspensions at 25°C in deionized water

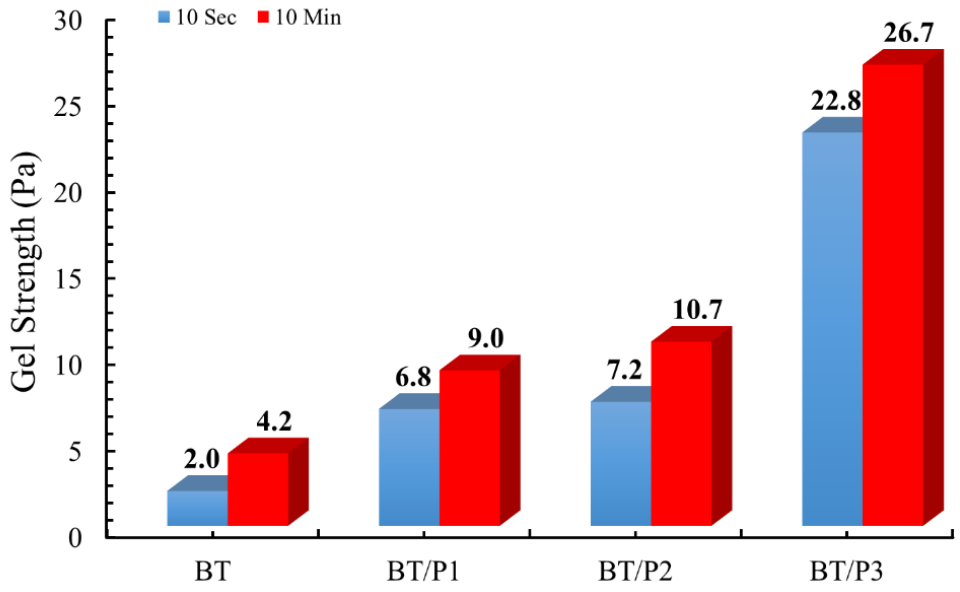

Figure 5.8 Gel strength of bentonite and bentonite/polymer suspensions at 85°C in deionized Water

5.3 Thermal stability of bentonite/polymer dispersions

The flow stability test was performed to study the viscosity of bentonite and bentonite/polymer dispersions at 25°C and 85°C with a constant shear rate (10 s^{-1}) for 2 hours. Figure 5.9 represents the viscosity vs time curves for bentonite and bentonite/polymer dispersions at 25°C. The addition of polymers in bentonite dispersion sufficiently improves the viscosity of bentonite dispersion. Bentonite dispersion represents the low viscosity while bentonite/polymer dispersion shows higher viscosities. The viscosities follow the trend BT< BT/P1<BT/P2<BT/P3 at 25°C and no meaningful change in viscosities were observed over the entire range on time. The highest viscosity was observed for BT/P3 dispersion that shows favorable behavior for drilling fluids. Figure 5.10 represents the viscosity vs time curves for bentonite and bentonite/polymer dispersions at 85°C. The curves follow the same trend of increase in viscosity at an elevated temperature as observed at 25°C. The viscosity of bentonite and bentonite/polymer dispersion increased at 85°C compared to low-temperature

viscosity values. This increment of viscosities was attributed to the flocculation of bentonite and bentonite/polymer dispersions. The highest viscosity was observed for BT/P3 dispersion at 85°C. With the increase in time, the viscosity of BT/P3 dispersions increases slightly and then becomes constant.

Thermal stability of bentonite/polymer dispersions is tested by aging at 90°C for 16 hours. The rheological properties and filtration properties of all the formulations are compared before and after aging at 25°C. The comparison of rheological and filtration properties of all the formulations are listed in Table 5.2. The constituents of drilling fluids are strongly affected by the elevated temperatures in deep wells. The main component of all the formulations is bentonite that is stable at elevated temperature but it shows flocculation which results in the increase in rheological properties such as yield stress. On contrary, the elevated temperature for bentonite dispersion leads to the high volume of fluid loss compared to the low temperature.

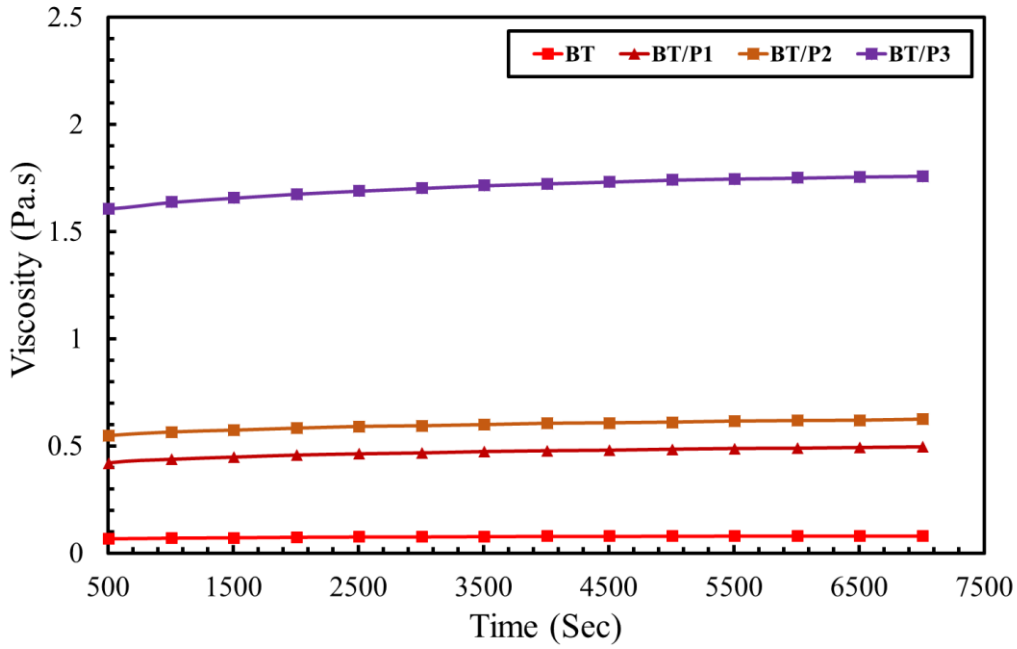

Figure 5.9 Comparison of viscosities of bentonite and bentonite/polymer suspensions at 25°C in deionized water

For bentonite/polymer dispersions, the rheological properties after aging are slightly increased indicating the flocculation during the aging process. Rheological data was fitted to the Herschel-Bulkley model to study the non-Newtonian behavior of drilling fluids. The yield stress of all the formulations slightly increased after the aging process indicating the dominant response of bentonite/polymer flocculation. The yield stress of bentonite and bentonite/polymer dispersions before and after aging follow the given trend BT< BT/P1<BT/P2<BT/P3. The consistency coefficient 'K' increases from BT dispersion to BT/P3 dispersions before and after aging but after aging 'K' values are slightly greater due to the flocculation. the. The higher values of 'K' for BT/P3 dispersion indicates that shear stress is strongly dependent on shear rate. The high 'K' values also describe that the well cleaning efficiency is better compared to the formulation which has low 'K' values. The flow behavior index 'n' indicates the shear thinning (pseudo-plastic) behavior for all the formulations before and after aging. But the flow behavior index 'n' has slightly higher values for the formulations after aging which indicates that the formulations before aging are more shear thinning (pseudo-plastic) in behavior.

Table 5.2 Rheological (Herschel-Bulkley model) and filtration characteristics of bentonite and bentonite/polymer suspensions before and after thermal aging

Formulations	Before Aging					After Aging				
	YS (Pa)	K ($Pa.s^n$)	n	GS 10 sec (Pa)	GS 10 min (Pa)	YS (Pa)	K ($Pa.s^n$)	n	GS 10 sec (Pa)	GS 10 min (Pa)
BT	0.83	2.8e-4	1.48	0.39	0.67	0.96	0.066	0.81	0.67	1.1
BT/P1	3.18	0.58	0.68	2.82	2.95	3.19	0.266	0.75	2.83	3.03
BT/P2	3.25	0.91	0.63	3.69	4.31	3.28	0.594	0.68	3.65	4.59
BT/P3	13.7	1.11	0.69	11.5	13.9	19.62	0.754	0.75	14.34	16.1

YS = yield stress, K= consistency coefficient, n = flow behaviour index, GS = gel strength, FL = fluid loss

The 10-seconds and 10-minutes gel strengths were measured for all the formulations before and after aging which are presented in Table 5.2. The gel strength of formulations after aging was slightly increased due to the flocculation or the enhanced interactions of bentonite with polymer molecules. The order of 10-seconds and 10-minutes gel strength before and after aging follows the given trend BT< BT/P1<BT/P2<BT/P3.

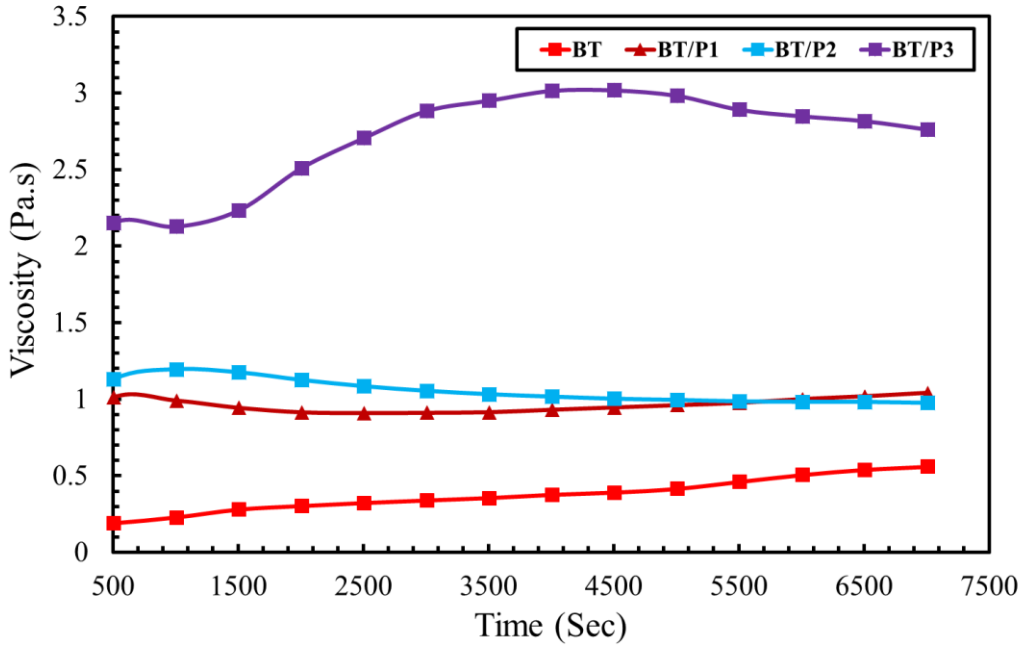

Figure 5.10 Comparison of viscosities of bentonite and bentonite/polymer suspensions at 85°C in deionized water

5.4 Filtration measurements

The API fluid loss test for all drilling formulations was performed at 25°C before and after aging at 90°C to determine the filtration performance. For all formulations, the filtrate had no color, which demonstrates that the filtrate was mainly water. The effect of different polymers on filtration performance without aging is shown in Figure 5.11. It was noticed that in the initial 5 minutes, the

filtration rate was considerably high. This high filtration rate was ascribed to the absence of filter cake in the start of filtration experiment. After 5 minutes, the rate of filtration was prominently decreased due to the formation of the filter cake. Bentonite dispersion showed the highest fluid loss compared to other bentonite/polymer dispersions. In bentonite filtration experiment, the filter cake had small pores and channels which allowed to penetrate the water through it giving high filtrate volume. The addition of polymers into bentonite dispersions distinctly decreased the rate of filtration and total fluid loss. The decreased fluid loss for bentonite/polymer dispersion was ascribed to the adsorption of polymer molecules on bentonite platelets. The long chain polymer molecules offer considerable hindrance in penetrating water through filter cake and it also forms a thin layer with blocking the pores of the filter cake.

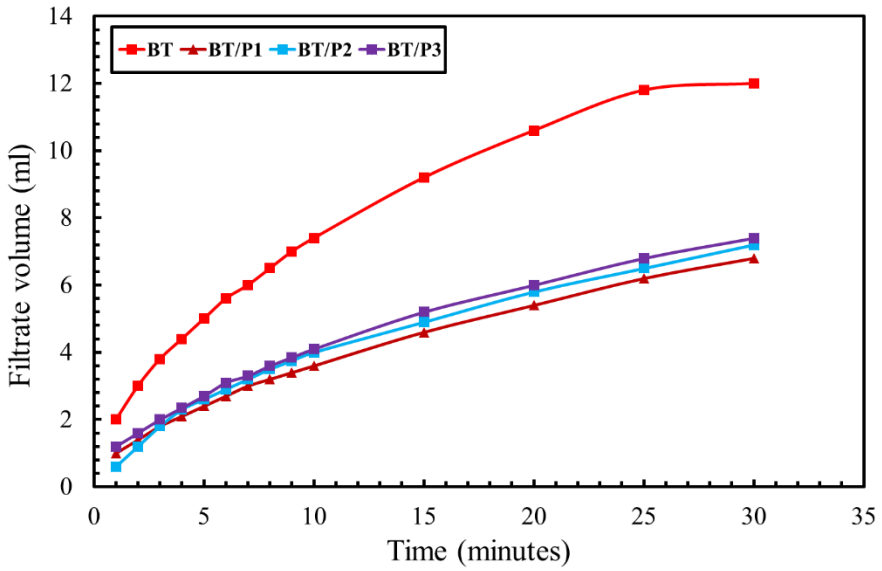

Figure 5.11 Fluid loss volume vs time before aging for bentonite and bentonite/polymer dispersions

The effect of polymers on the filtration performance after aging is shown in Figure 5.12. The filtration performance of the bentonite and bentonite/polymer dispersions showed similar trend but with a higher value of fluid loss volume of aged samples. The rate of filtration of bentonite and

bentonite/polymer dispersions was considerably high in the initial 5 minutes. However, after 5 minutes, a sudden drop in the rate of filtration was observed due to the formation of the filter cake. The fluid loss volume of bentonite dispersion was increased after aging the bentonite dispersion. The aging process induces the flocculation among bentonite platelets and adsorbed water on bentonite was given out which increased the filtrate volume. The performance of bentonite/polymer dispersions (aged) was slightly decreased compared to the bentonite/polymer dispersions (without aged). The aging of formulation induces the flocculation which resulted in the increase in filtrate volume. The comparison of total fluid loss volume per 30 minutes for all the formulation before aging and after aging is presented in Figure 5.13. It indicates that incorporation of polymer in bentonite dispersion enhances the filtration performance of drilling fluids. Further, the aging of drilling fluid formulations severely affects the filtration performance of bentonite dispersions but it has a slightly less effect on bentonite/polymer dispersions.

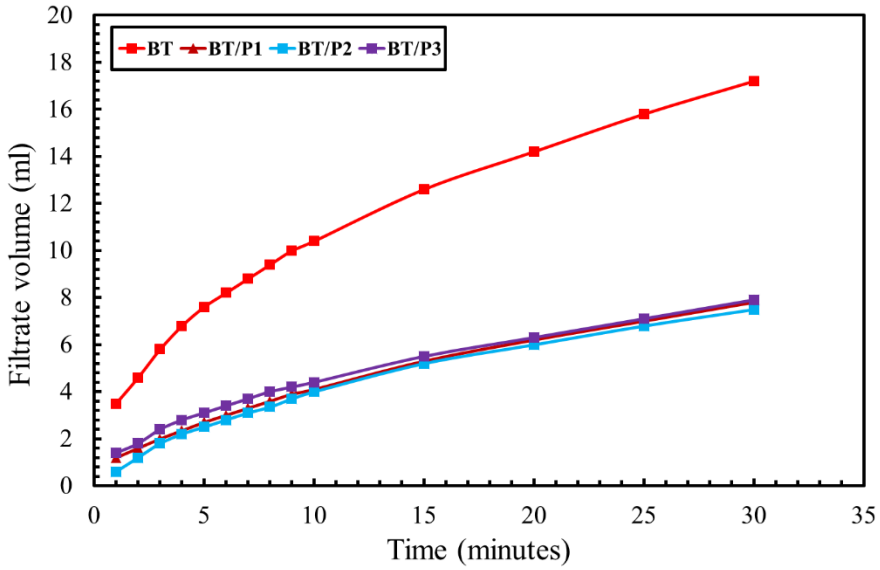

Figure 5.12 Fluid loss volume vs time after aging for bentonite and bentonite/polymer dispersions

The overall filtration results showed that the addition of polymer in bentonite dispersion would sufficiently reduce the filtration volume. As the DOH of polymer chains increases, the interactions of polymer chains with positively charged edges of bentonite increases which results in the slight increase in fluid loss. The acrylamide-based copolymers containing bulky comonomers showed slightly better filtration properties compared to the copolymer containing smaller comonomers. However, the effect of DOH and comonomers size has not significant effect on filtration properties and all polymers showed similar filtration properties before and after aging.

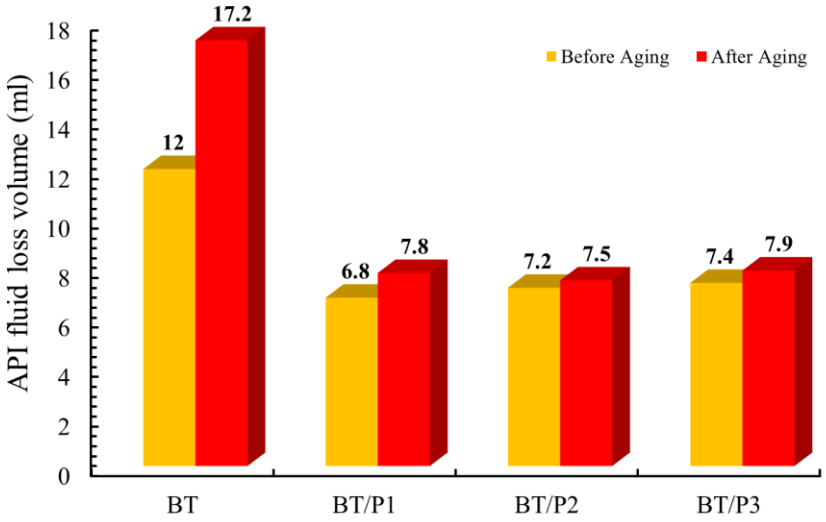

Figure 5.13 Total fluid loss volumes of bentonite and bentonite/polymer suspensions at 25°C before and after aging

CHAPTER 6

Rheological and filtration properties of clay-polymer systems:

Impact of polymer structure

The discussion of this chapter is divided into four different sections. The first section describes the rheological properties of the copolymer (P1) and terpolymer (P4) in deionized and salt water at 25°C and 85°C. The second and third section explains the rheological behavior of BT and BT/polymer dispersions at 25°C and 85°C in deionized and salt water and gel strength of drilling fluid formulations. The fourth section represents the filtration characterizes of BT and BT/polymer dispersions at 25°C in deionized and salt water.

6.1 Rheological properties of polymer solutions

Figure 6.1 and Figure 6.2 represents the viscosity profiles of polymer P1 and polymer P4 at 25°C and 85°C respectively in the presence of deionized and salt water. All the polymer solutions present pseudoplastic (shear thinning) behavior at both temperatures. The steady shear viscosities of polymer solutions are distinct from each other based on the polymer structure, the chemical structure of monomer in the backbone, charge distribution in monomer groups and their distribution along the polymer chain. The presence of electrolyte in polymer solution and temperature also affects the shear viscosity of polymer solutions. All the polymer solutions in deionized and salt water showed non-Newtonian behavior as the increase in the shear rate causes a deacrease in the viscosity of the polymer solutions. In Figure 6.1, the polymer solution P4 showed maximum shear viscosity compared to the P1 polymer solution in deionized water due to the presence of three distinct monomers in the polymer

chain. When copolymer and terpolymer dissolved in water separately, the functional groups along the backbone of polymer chains get hydrolyzed and becomes negatively charged. These negatively charged functional groups induce repulsive forces between the monomers (segments) of the same polymer chain and as a results polymer chains starts swelling. The combined effect of repulsive forces and swelling of polymer chains results in the increase in viscosity. The polymer solution P4 has three distinct monomers such as AM, AMPS and NVP monomers in the backbone of the polymer chain. The first two monomers (AM and AMPS) hydrolyzed in water giving the negative charge on their functional groups and third monomer (NVP) also has a partial negative charge on it. The maximum shear viscosity of P4 polymer solution is due to the enormous number of repulsive forces compared to the P1 polymer solution.

The presence of electrolyte in polymer solutions affects the shear viscosity. The polymer solution P4/S showed high shear viscosity compared to the polymer solution of P1/S. The presence of monovalent cations produced by (NaCl) solution offers considerable shielding to the negatively charged functional of polymer chains. Consequently, the interaction between cations and negatively charged functional groups arises and repulsive forces among the negatively charged functional declines, then polymer chains start to coil up and giving the decreased viscosity of polymer solutions. Figure 6.2 shows that the increase in temperature of the polymer solutions up to 85°C decreased the viscosity of polymer solutions compared to the polymer solutions at 25°C. The decrease in viscosity was attributed to the reduction of repulsive forces among the polymer chains and mobility of polymer chains enhanced at higher temperature which results in the decrease in viscosity.

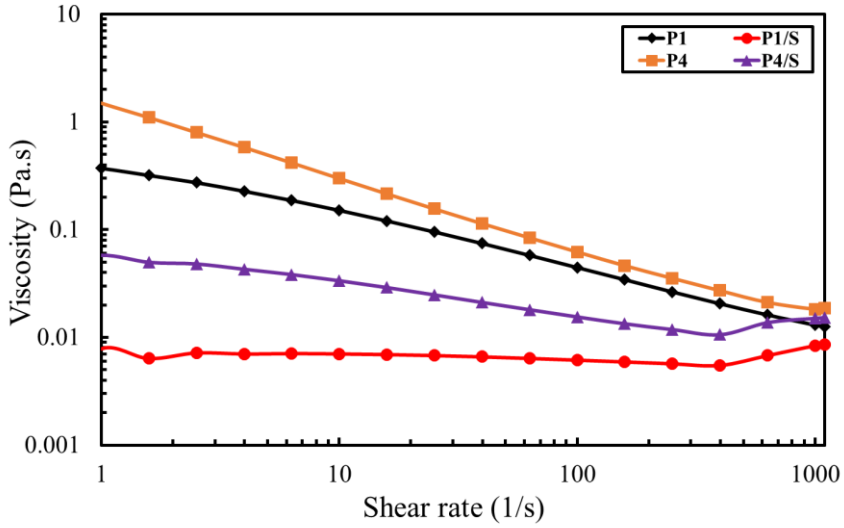

Figure 6.1 Steady shear viscosity of polymer solutions at 25°C in deionized and salt water

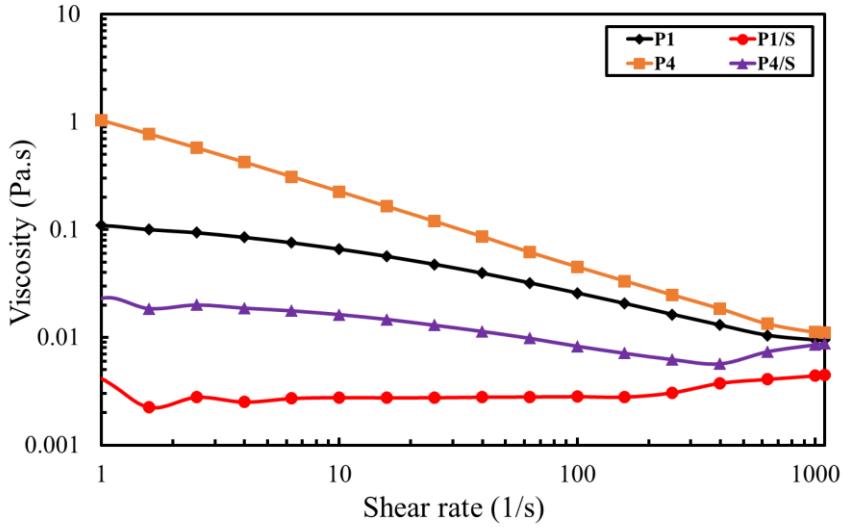

Figure 6.2 Steady shear viscosity of polymer solutions at 85°C in deionized and salt water

The flow curves of polymer solutions at 25°C and 85°C in deionized and salt water are represented in Figure 6.3Figure 6.3 and Figure 6.4. In Figure 6.3, the polymer solution P4 has higher shear stress compared to the polymer solution P1 at 1 s^{-1} shear rate in deionized water. Similarly, the polymer solution P4/S has higher shear stress compared to the polymer solution P1/S at 1 s^{-1} shear rate in salt

water. The shear stress changes more prominently at low shear rate due to the strong repulsive interactions among the polymer chains. While at high shear rates, the change in shear stress was not prominent due to the alignment of polymer chains along the direction of flow. In Figure 6.4, the similar trend of shear stress of polymer solutions was observed in deionized and salt water at 85°C. But the overall shear stress of polymer solution decreases at 85°C compared to the 25°C due to the increased mobility of polymer chains and fewer interactions among the polymer chains.

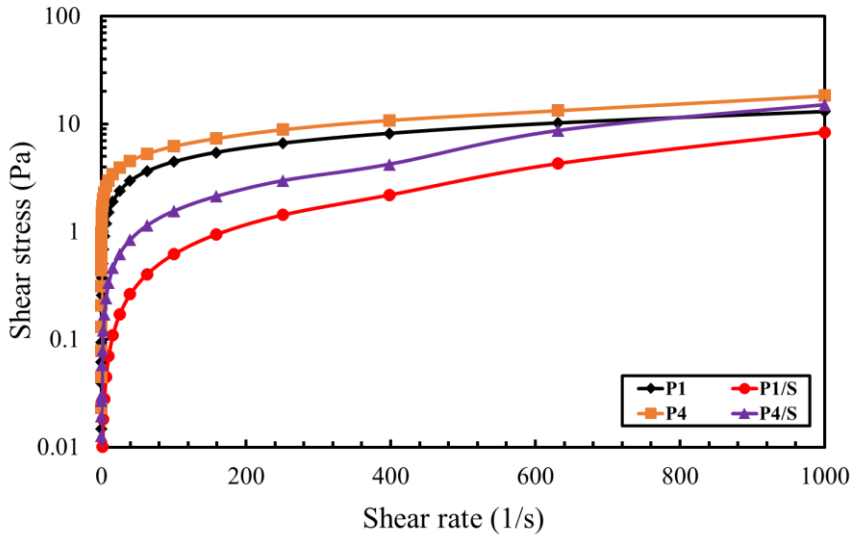

Figure 6.3 Flow curves of polymer solutions at 25°C in deionized and salt water

In summary, the rheological properties of polymer solutions in deionized and salt water suggest that terpolymer (P4) comprising of AM, APMS and NVP monomers have a higher viscosity in deionized water at 25°C and 8°5C compared to the copolymer (P1) of AM and APMS. The presence of NVP monomer in terpolymer imparts the additional interactions among the polymer chains which enhanced the viscosity of polymer solutions. Further, NVP monomer is less affected by the presence of electrolyte solution at both temperatures. After measuring the rheological properties of copolymer and terpolymer in deionized and salt water at 25°C and 85°C, we were additionally interested to see

how these polymers interact with polymers in deionized and salt water. Further details of rheological measurements of BT/polymer dispersions are presented in next section.

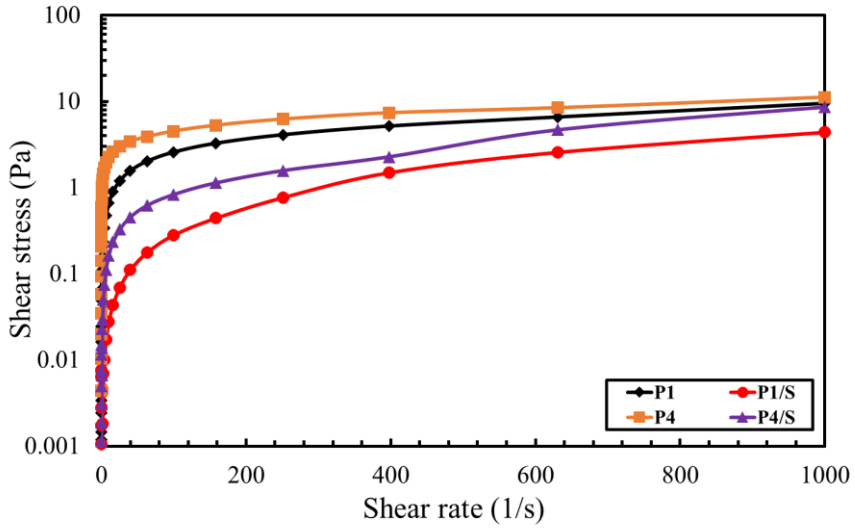

Figure 6.4 Flow curves of polymer solutions at 85°C in deionized and salt water

6.2 Rheological properties of drilling fluid formulations

The rheological properties of BT and BT/polymer dispersions were investigated in deionized and salt water at 25°C and 85°C. Figure 6.5 indicates the steady shear viscosity of BT and BT/polymer dispersions at 25°C in deionized and salt water. The incorporation of the copolymer (P1) and terpolymer (P4) in BT dispersion enhanced the rheological properties. The minimum steady shear viscosity of BT dispersion was ascribed to the weak inter-particle interactions of BT platelets in deionized and salt water. The enhanced rheological properties of BT/polymer dispersions by the inclusion of copolymer (P1) and terpolymer (P4) in BT dispersion could be explained by the interactions among BT platelets and polymer chains. The positively charged edges of BT platelets interact with the negatively charged moieties along the backbone of polymer chains. The polymer

P4 has three distinct moieties along the backbone compared to the polymer P1 and makes strong interactions with positively charged edges of BT resulting the highest steady shear viscosity of BT/P4 dispersion in Figure 6.5. The BT/P1 dispersion showed less steady shear viscosity compared to the BT/P4 dispersions due to the less number of interactions among BT platelets and negatively charged moieties of polymer (P1).

The presence of electrolyte in BT and BT/polymer dispersion results in the decrease in steady shear viscosity. The electrolyte solution produces metal cations in the BT dispersion and BT/polymer dispersions. In BT dispersion, metal cations shrink the double layer of charges around the BT platelets releasing the adsorbed water on BT platelets and result in the increase in flocculation of BT platelets. The enhanced flocculation consequently decreased the steady shear viscosity of BT/salt (S) dispersion. The inclusion of electrolyte in BT/polymer dispersion also affects the steady shear viscosity of dispersions. The metals cations produced by electrolyte offers considerable screening to the negatively charged moieties along the backbone of polymers and restricts the interactions of polymer functional group with BT platelets. The BT/P4/S dispersion showed high steady shear viscosity compared to the BT/P1/S dispersion because of the presence of NVP monomer in P4 polymer which shows high stability towards the salinity. All these results are impressive and support the results that were observed for polymer solutions in deionized and salt water.

The steady shear viscosities of BT and BT/polymer dispersions in deionized and salt water at 85°C are presented in Figure 6.6. The rise in temperature of BT dispersions increases the steady shear viscosity slightly because of thermal induce swelling and flocculation of BT platelets. Likewise, the rise in temperature of BT/polymer dispersions to 85°C results in the rise in steady shear viscosity compared to the BT/polymer dispersions at 25°C. At 85°C in deionized water, the BT/P4 dispersion

shows maximum steady shear viscosity compared to the BT and BT/P1 dispersion. Similarly, BT/P4/S dispersion shows maximum steady shear viscosity at 85°C in salt water compared to the BT/S and BT/P1/S dispersions. In summary, NVP monomer based terpolymer (P4) showed excellent rheological properties in BT/polymer dispersions compared to the AMPS monomer based copolymer (P1) at 25°C and 85°C in the presence of deionized and salt water. The NVP monomer provides excellent stability towards the salinity and temperature which results in the enhanced rheological properties.

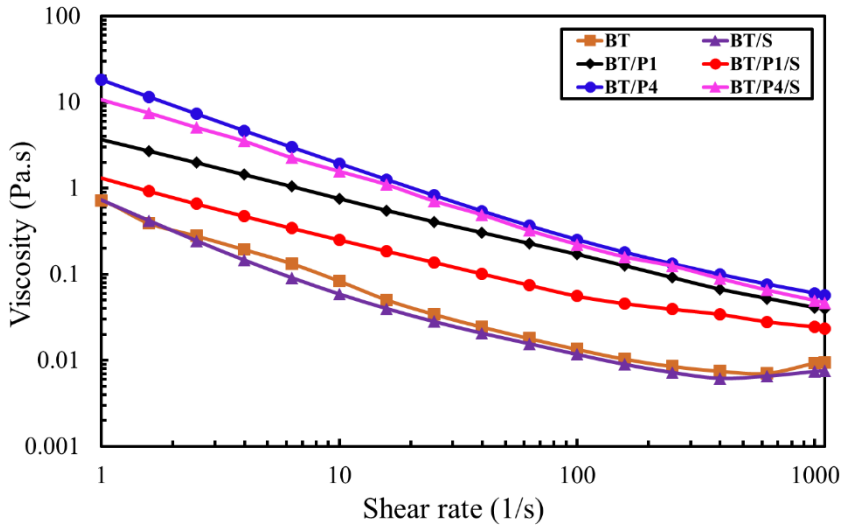

Figure 6.5 Viscosity profiles of BT and BT/polymer dispersions at 25°C in deionized and salt water

The flow curves of BT and BT/polymer dispersions are represented in and Figure 6.7 and Figure 6.8 at 25°C and 85°C in deionized and salt water, respectively. All the flow curves of BT and BT/polymer dispersions exhibit non-Newtonian behavior at 25°C and 85°C. In Figure 6.7, the shear stress of BT dispersion has a minimum value at 25°C compared to the BT/polymer dispersions. The addition of polymers in BT dispersion exhibits the considerable increase in shear stress of BT/polymer due to the interactions of negatively charged moieties in the polymer chains and BT

platelets. BT/P4 dispersion displayed maximum value of shear stress in deionized water compared to the BT dispersion and BT/P1 dispersion.

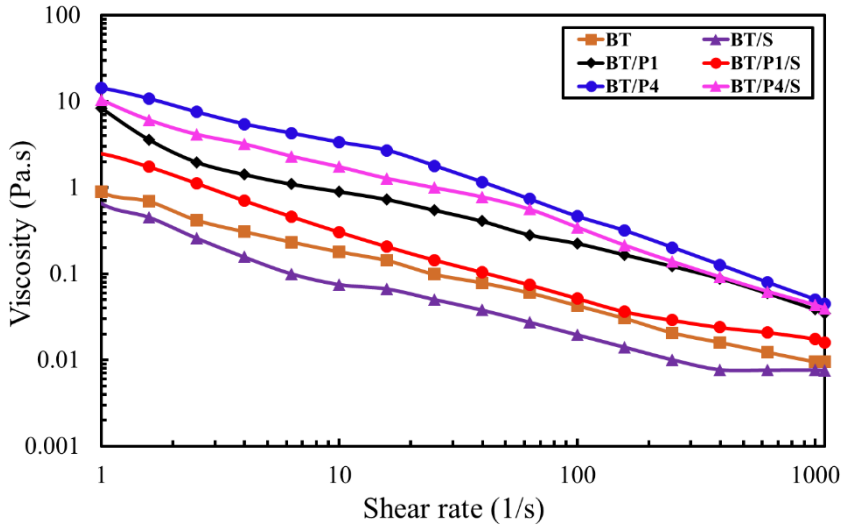

Figure 6.6 Viscosity profiles of BT and BT/polymer dispersions at 85°C in deionized and salt water

The presence of electrolyte affects the shear stress of BT and BT/polymer dispersions. The metal cations produced by the electrolyte solution hinders the attraction among polymer moieties and BT platelets and BT/polymer dispersion exhibit slightly lower value of shear stress. In the presence of an electrolyte, BT/P4/S showed highest shear stress compared to the BT/S and BT/P1/S dispersion. The order of shear stress of all the dispersions are presented as BT/P4>BT/P4/S>BT/P1>BT/P1/S> BT>BT/S. In Figure 6.8, the shear stress of all the dispersions are presented at 85°C in deionized and salt water. The higher temperature shear stress of all the dispersions follows the same trend as presented at 25°C but with the slight increase in shear stresses of all the dispersions. The polymer P1 and P4 are stable at elevated temperature but the slight increase in shear stress at high temperature was attributed to the flocculation of BT platelets due to thermal induce swelling in BT/polymer dispersions.

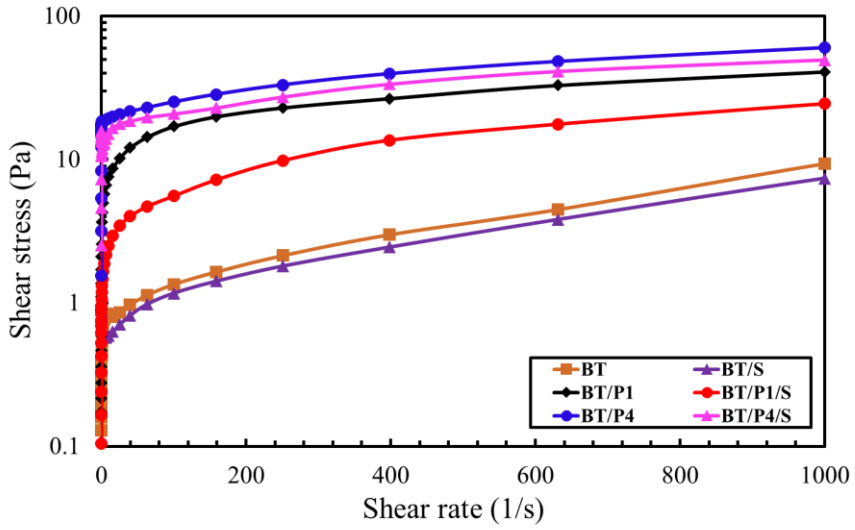

Figure 6.7 Flow curves of BT and BT/polymer dispersions at 25°C in deionized and salt water

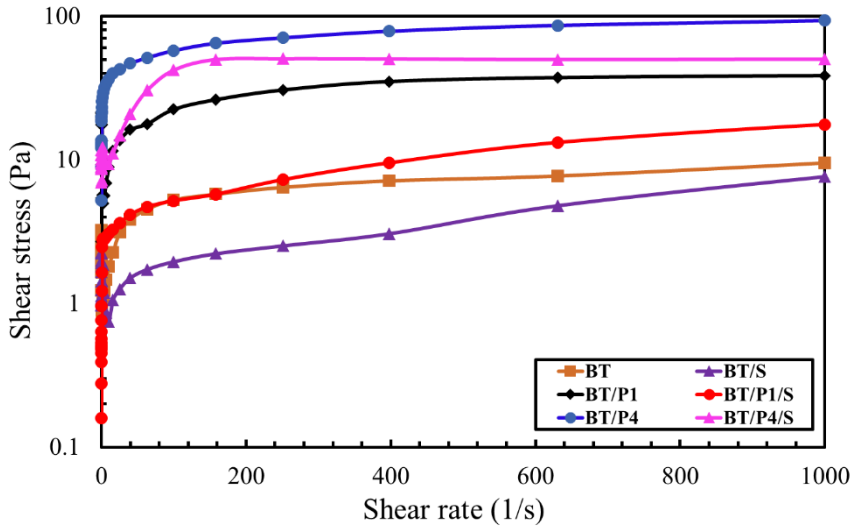

Figure 6.8 Flow curves of BT and BT/polymer dispersions at 85°C in deionized and salt water

The experimental data of shear stress vs shear rate was fitted to the Herschel-Bulkley model to study non-Newtonian behavior at 25°C and 85°C in deionized and salt water. The rheological parameters such as yield stress, consistency coefficient ‘k’ and flow behavior index ‘n’ obtained from Herschel-Bulkley model for BT and BT/polymer dispersions are presented in Table 6.1. The yield stress of

BT and BT/polymer dispersion explained the attractive forces among the particles and defines the ability of drilling fluid to lift the drilled cutting from the wellbore. It was observed that the inclusion of polymers in BT dispersion significantly enhanced the yield of stress of BT/polymer dispersions in deionized and salt water. The rise in temperature from 25°C to 85°C increase the yield stress of all BT and BT/polymer dispersions due to the interparticle flocculation of BT platelets. At 25°C, the yield stress of BT/P4 and BT/P1 dispersion increased compared to the yield stress of BT dispersion in deionized water. Similarly, at 85°C the yield stress of BT/P4 and BT/P1 dispersion increased compared to the yield stress of BT dispersion in deionized water.

The presence of electrolyte considerably affects the yield stress of all BT and BT/polymer dispersions. The yield stress of BT/P4/S dispersion decreases 5.8% and 6.3% at 25°C and 85°C respectively compared to the BT/P4 dispersion. Similarly, the yield stress of BT/P1/S dispersion decreased 39% and 50% at 25°C and 85°C respectively compared to the BT/P1 dispersion. In Table 6.1, consistency coefficient 'k' and flow behavior index 'n' of BT and BT/polymer dispersion are presented at 25°C and 85°C in deionized and salt water. Consistency coefficient shows the dependence of shear stress on shear rate and defines the hole cleaning efficiency of drilling fluids. The highest value of consistency coefficient was observed for BT/P4 and BT/P4/S dispersions at 25°C and 85°C. It was observed that all the BT and BT/polymer dispersions have flow behavior index 'n' less than unity which indicates the shear thinning (pseudoplastic) behavior of all the formulations. The fascinating fact was observed about flow behavior index which indicates that by the increase in temperature, the pseudo-plastic behavior of all the formulations increases.

Table 6.1 Rheological parameters of BT and BT/polymer dispersions in deionized and salt water at 25°C and 85°C

Dispersions	Yield stress τ_o (Pa)		Flow behavior index (n)		Consistency coefficient K (Pa. s^n)	
	25°C	85°C	25°C	85°C	25°C	85°C
BT	0.36	1.16	0.60	0.64	0.084	0.69
BT/S	0.33	0.67	0.68	0.77	0.065	0.26
BT/P1	1.86	3.85	0.38	0.61	0.349	0.55
BT/P1/S	1.13	1.93	0.64	0.79	0.266	0.40
BT/P4	14.15	15.9	0.61	0.54	1.31	1.84
BT/P4/S	13.33	14.9	0.55	0.60	0.98	1.25

In summary, the rheological properties of BT dispersion enhanced significantly by adding copolymer (P1) and terpolymer (P4). The rheological properties such as viscosity and yield stress significantly improved using polymers. The excellent rheological properties of BT/P4 and BT/P4/S dispersions are observed due to the addition of P4 polymer in BT dispersion in deionized and salt water at 25°C and 85°C which makes it suitable additive for high temperature and high salinity applications of drilling fluids. The exceptional rheological properties of BT/P4 and BT/P4/S dispersions are observed due to the strong interactions of P4 polymer (terpolymer) with BT platelets and the presence of NVP monomer in P4 polymer which improves the stability towards high temperature and salinity.

6.3 Gel strength of drilling fluid formulations

Gel strength of drilling fluids describes the capability to suspend the drilled cuttings in the drilling process. Various parameters affect the gel strength of water-based drilling fluids such as salts, acidic gases, additives in the drilling fluids, amount and size of solid contents and most importantly the temperature. In this study, the effect of temperature and electrolyte on gel strengths of BT and BT/polymer dispersions were studied. The gel strength of BT and BT/polymer dispersions were measured in deionized and salt water at 25°C and 85°C. The inclusion of a polymer in BT dispersion enhanced the 10-seconds and 10-minutes gel strength significantly at both temperatures. The gel

strength of BT and BT/polymer dispersions in deionized and salt water at 85°C have higher values compared to the gel strength of BT and BT/polymer dispersions at 25°C. The enhanced gel strength at elevated temperature was attributed to the interactions among polymer molecules and BT platelets.

The incorporation of electrolyte in BT and BT/polymer dispersions affects the gel strength at both temperatures. The metal cations produced by electrolyte screens negatively charged moieties of polymer chains thus reducing the interactions among BT platelets and polymer molecules. Consequently, the gel strength of BT and BT/polymer dispersions were affected by the presence of an electrolyte (NaCl). Table 6.2 represents the 10-seconds and 10-minutes gel strength of BT and BT/polymer dispersions in deionized and salt water at 25°C and 85°C. At 25°C, the 10-seconds and 10-minutes gel strength of BT/P4 dispersion increased 2840% and 2300%, respectively, compared to the BT dispersion. Similarly, 10-seconds and 10-minutes gel strength of BT/P1 dispersion increased is 860% and 728%, respectively compared to the BT dispersion. In the presence of an electrolyte, the 10-seconds and 10-minutes gel strength of BT/P4/S dispersion decreased 23% and 18%, respectively, compared to the BT/P4 dispersion. The 10-seconds and 10-minutes gel strength of BT/P1/S dispersion decreased 65% and 63%, respectively, compared to the BT/P1 dispersion.

At 85°C, the 10-second and 10-minute gel strength of BT/P4 dispersion increased 815% and 431% respectively compared to the BT dispersion. Furthermore, 10-seconds and 10-minutes gel strength of BT/P1 dispersion the increased is 245% and 112% respectively compared to the BT dispersion. In the presence of an electrolyte, the 10-seconds and 10-minutes gel strength of BT/P4/S dispersion decreased 25% and 20% respectively compared to the BT/P4 dispersion. The 10-seconds and 10-minutes gel strength of BT/P1/S dispersion decreased 30% and 37% respectively compared to the BT/P1 dispersion.

In summary, the gel strengths follow the order BT/S<BT<BT/P1/S<BT/P1< BT/P4/S< BT/P4 at low and high temperature. The higher value of gel strength of BT/P4 dispersion is attributed to the strong interactions of BT and P4 polymer due to the presence of NVP monomer in the backbone of polymer chains. The presence of NVP monomer improves the thermal stability at elevated temperature and high salinity and offers considerable electrostatic attractions towards BT platelets. Therefore, high values of gel strengths of BT/P4 and BT/P4/S suggest that P4 polymer would be a suitable candidate for high temperature and high salinity applications of drilling fluids.

Table 6.2 Gel strengths of BT and BT/polymer dispersions at 25°C and 85°C in deionized and salt water

Dispersions	Gel strength (Pa) at 25°C		Gel strength (Pa) at 85°C	
	10-sec	10-min	10-sec	10-min
BT	0.5	0.7	2	4.2
BT/S	0.38	0.52	1.3	2.3
BT/P1	4.8	5.8	6.9	8.9
BT/P1/S	1.85	2.13	4.8	5.6
BT/P4	14.7	16.8	18.3	22.3
BT/P4/S	11.3	13.7	13.7	17.8

6.4 Filtration characteristics of drilling fluid formulations

API filtration experiments for all BT and Bent/polymer dispersions were carried out at 25°C in the presence of deionized and salt water. All the BT and BT/polymer dispersions filtrate had no color which exhibits that filtrate was chiefly water. The effect of salinity and polymers on filtration performance of BT and BT/polymer dispersions is presented in Figure 6.9. The initial fluid loss into the formation during first 5 to 7 minutes is known as spurt loss. During the spurt loss, the rate of fluid loss in the formation is usually high because of the absence of filter cake. The filter cake formed

during the initial spurt loss in the formation. In Figure 6.9, it was observed that the rate of fluid loss of filtration experiment was high in the initial 5 minutes and subsequently the rate of fluid loss declined due to the formation of the filter cake. In deionized water, BT dispersion showed maximum fluid loss compared to the other BT/polymer dispersions. The incorporation of polymers in BT dispersion explicitly reduced the fluid loss and rate of filtration. The fluid loss of BT/P4 and BT/P1 dispersions was reduced 32% and 40%, respectively, compared to the BT dispersion. In electrolyte solution, BT/S dispersion showed maximum fluid loss compared to the BT/S/polymer dispersions. The fluid loss of BT/P4/S and BT/P1/S was reduced 68% and 72% respectively compared to the BT/S dispersion.

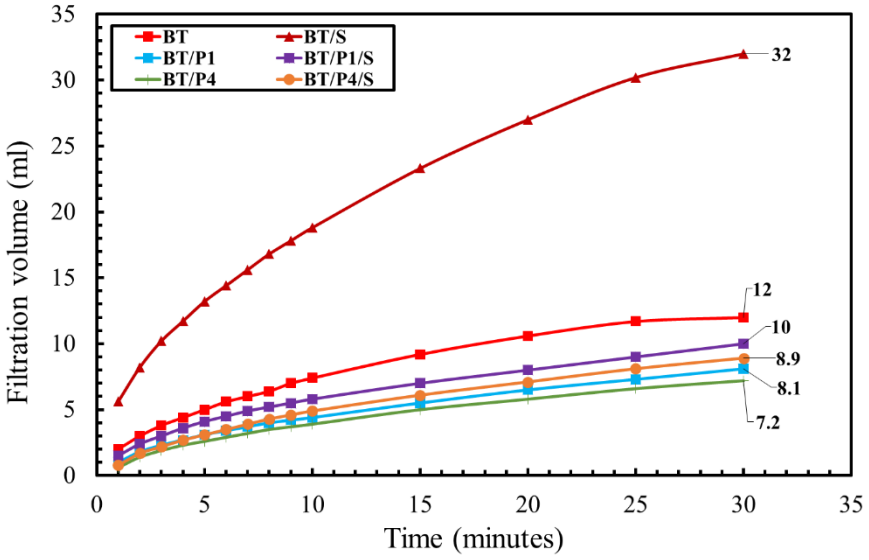

Figure 6.9 Fluid loss vs time profiles of BT and BT/polymer dispersions at 25°C in deionized and salt water

Filter cakes were obtained after filtration experiments. The prominent features of filter cakes include compactness, smoothness, thickness and surface texture. Figure 6.10 represents Digital photographs of filter cakes were taken after immediately filtration experiments. The surface texture shows that the addition of polymer produces smooth and defect free filter cakes. Filter cake thicknesses were

presented in Table 6.3, which shows that BT/P4 dispersion produced minimum filter cake thickness. Minimum filter cake thickness is one of the desired features for efficient and smooth drilling operations and it also reduces the pipe sticking problem

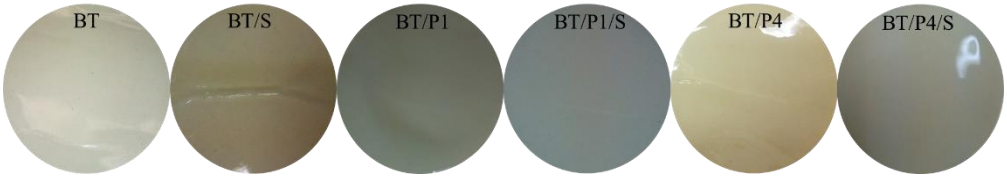

Figure 6.10 Digital photographs of filter cakes taken immediately after filtration experiments

Table 6.3 Filter cake thickness of BT and BT/polymer dispersions in deionized and salt water

Formulations	BT	BT/S	BT/P1	BT/P1/S	BT/P4	BT/P4/S
Filter cake thickness (mm)	2.04	1.45	1.38	1.1	1.19	1.8

In summary, the filtration experiments showed that incorporation of polymers in BT dispersion reduced the filtrate volume significantly. The polymer which contains NVP monomer in the backbone showed an excellent reduction in fluid loss for Bent/P4 and Bent/P4/S dispersion. If Bent/polymer dispersion has superior rheological properties, then it will produce minimum filtrate volume. The filtration experiment results were also supported by rheological experimental results which exhibited that Bent/P4 in deionized water and Bent/P4/S dispersion in salt water have superior rheological properties.

CHAPTER 7

Investigation of polymer and nanoparticles impact on rheology, fluid loss and filter cake properties

7.1 Rheological properties of drilling fluids

The optimization of rheological properties of drilling fluids such as apparent viscosity, plastic viscosity, gel strength and yield point are very important for smooth drilling operation. These properties can be controlled by adding various drilling fluid additives such as viscosifiers, pH control agents, fluid loss agent, and rheological modifiers to the water base drilling fluids. Water based drilling fluids are shear thinning (Non-Newtonian) in nature, which shows the decrease in viscosity of drilling of drilling fluids with the increase in shear rate. The high gel strength of drilling required for suspending drilled cutting during the intermittent drilling process. Yield point describes the interactions among the particles of drilling fluid additives, which means that strong interaction among the additives of drilling fluid results high yield point of drilling fluid and high yield point of drilling fluids is required to transport the drilled cuttings to the surface. Investigation of Polymer and Nanoparticles Impact on Drilling Fluid Rheology, Fluid loss and Filter Cake Properties

In this section, the effect of different polymers and nanoparticles on the rheological properties of base fluid (bentonite dispersion in water) was studied. All the rheological properties were measured at 25°C and before measuring rheological properties all the drilling fluid formulations were subjected to the 10-minutes high shearing to get the homogenous dispersions for better results.

Figure 7.1 present the apparent viscosities of various drilling fluid formulations and it's an important property of drilling of drilling fluids that describes about thixotropy of drilling fluids. The BT dispersion (base drilling fluid) shows (7 Pa.s) apparent viscosity and addition of different nanoparticles (N1) and (N2) slightly affect the apparent viscosity (6.5 Pa.s) and (6 Pa.s) compare to the base drilling fluid. The decrease in apparent viscosity of base drilling fluid is due to the presence of nanoparticle that resist to make the interaction among bentonite particles and ultimately affected the apparent viscosity.

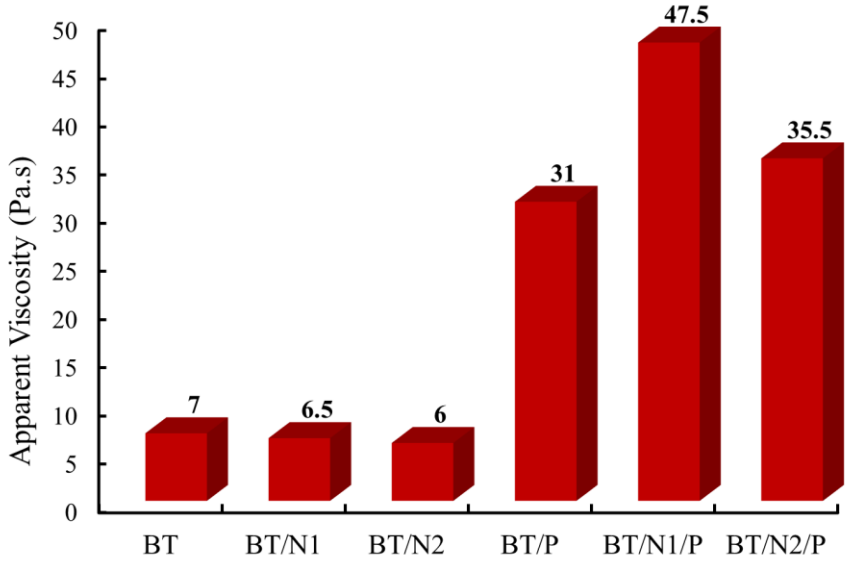

Figure 7.1 Apparent viscosity of drilling fluid formulations

The addition of polymer (P) has significant impact on the increment of apparent viscosity of base fluid. The increase in apparent viscosity of base drilling fluid by the addition of polymer is attributed to the presence of hydrophilic groups in polymer chain that attach with the water molecules present in the clay platelets. Secondly, the polymer chains adsorb on clay platelets and giving three-dimensional network of polymer-clay system that results the increase in apparent viscosity. The addition of polymer and nanoparticles has increased the apparent viscosity of base drilling fluid from

7 Pa.s to 47.5 Pa.s for BT/N1/P and 7 Pa.s to 35.5 Pa.s for BT/N2/P drilling fluid. Out of all the drilling fluid formulations, BT/N1/P shows superior results of apparent viscosity. Hence, the addition of polymer and nanoparticles in base drilling fluid increased the rheological properties such as apparent viscosity. However, high values of apparent viscosity should be in the controlled range for smooth and efficient drilling operation in oil and gas wells.

Figure 7.2 presents the plastic viscosity of drilling fluid formulations. The plastic viscosity of drilling fluid is affected by various parameters which include the weight of drilling fluid, temperature and presence of solid contents. Plastic viscosity represents the ability of drilling fluid to perform the drilling operation under high shear rates and its shear rate dependent. The problems associated the high plastic viscosity are high surge and swab pressure, high affinity of pipe sticking during the drilling operations, and high circulation density. Here the base drilling fluid shows 5 Pa.s plastic viscosity and addition of (0.8 g) of different nanoparticles to the based drilling fluid not affected the plastic viscosity of drilling fluid. While the addition of (0.4 g) of polymer to the base fluid increased the plastic viscosity of drilling fluid up to (40 Pa.s). The high plastic viscosity of BT/P drilling fluid may affect the smooth drilling operations. The addition of nanoparticles and polymer to the base drilling has raised the plastic viscosity compared to the base drilling fluid and decreased compared to the BT/P drilling fluid. In this study, the increase of plastic viscosity was observed in the range of (45-50 Pa.s) by the addition of polymer and nanoparticles. The selection of plastic viscosity values also depends on the drilling parameter of oil and gas well.

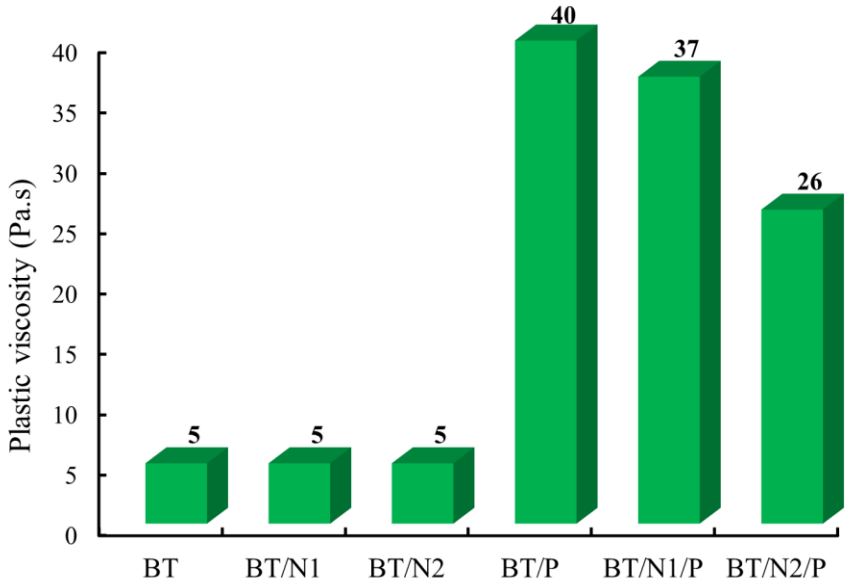

Figure 7.2 Plastic viscosity of drilling fluid formulations

Figure 7.3 represent the yield point of different drilling fluid formulations. Yield point of drilling is one of the important parameter that describes the ability of drilling of drilling fluid to transport the drilled cutting from the bottom hole to the surface. The high value of yield point is required for efficient better lifting capacity of drilled cuttings. If the yield value is out of range for the given deep well drilling operations, then it may cause pressure and swab fluctuations. In this study, the addition of nanoparticles (N1) and (N2) to base drilling fluid decreased the yield point of drilling fluid from 4 to 3 Pa for BT/N1 and 4 to 2 Pa for BT/N2 drilling fluid. While the addition of polymer in base drilling fluid has raised the yield point from 4 to 6 Pa for BT/P drilling fluid. This increase in yield point due to the addition of polymer is because of interaction among the bentonite platelets and hydrophilic groups in the polymer chains. The addition of nanoparticles and polymer to the base fluid also increased the yield point greatly from 4 to 21 Pa for BT/N1/P and 4 to 19 Pa for BT/N2/P drilling fluid. The increase values of yield point by the addition of polymer and nanoparticles is due to the adsorption of polymer chains on the platelets of clay minerals. The highest yield point value of BT/N1/P drilling fluid would be a suitable choice for drilling operations.

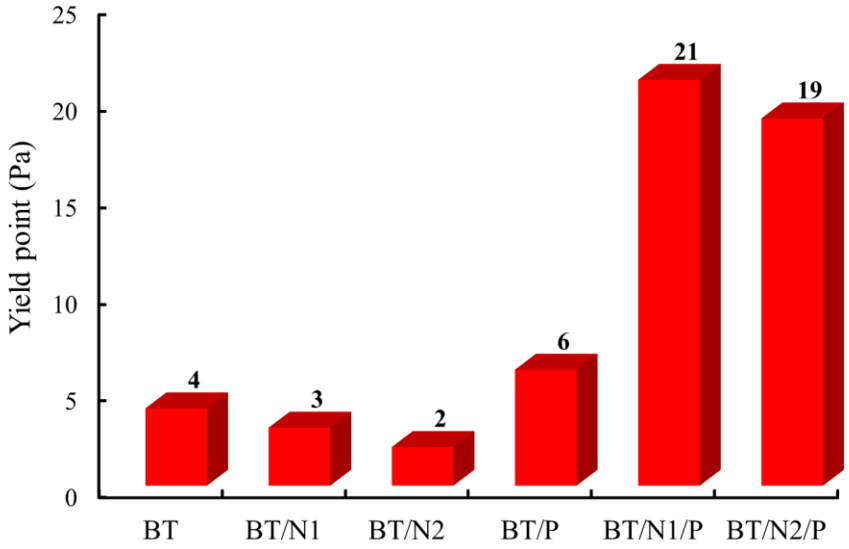

Figure 7.3 Yield point of drilling fluid formulations

Gel strength of drilling fluid is the ability to hold the drilled cuttings for specific period due to the intermittent drilling operations. Figure 7.4 presents the 10-sec and 10-min gel strengths of all drilling fluid formulations. The incorporation of nanoparticles such as N1 and N2 has not significantly increased 10-sec and 10-min gel strengths. The gel strengths of drilling fluid formulations also show the gelation among the drilling fluid additives. The addition of polymer (P) to the base drilling fluid raised the 10-sec gel strength from 2 to 8 Pa and 10-min gel strength from 4 to 23 Pa for BT/P drilling fluid. This increase of gel strength is due to the gelation forces among the clay minerals and hydrophilic groups of polymer chains. The incorporation of nanoparticles and polymer to base drilling fluid has more significant increase in the gel strengths compared to the base drilling fluid. The increase in 10-sec and 10-min gel strength (2 to 10) Pa and (4 to 25) Pa respectively, for BT/N1/P drilling fluid has observed compared to the base drilling fluid. While, the increase in 10-sec and 10-min gel strength (2 to 9) Pa and (4 to 16) Pa respectively for BT/N2/P drilling fluid has observed compared to the base drilling fluid. Among all the drilling fluid formulations, BT/N1/P drilling fluid formulation shows better values of gel strengths.

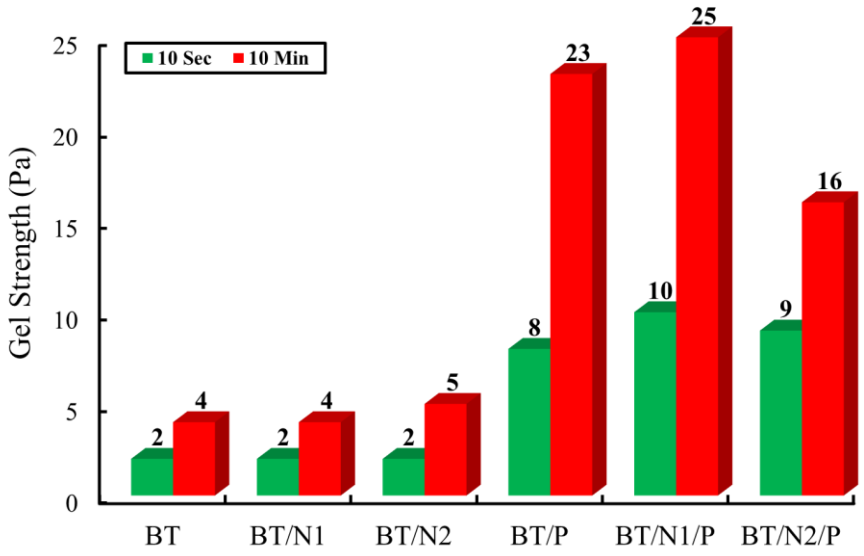

Figure 7.4 Gel strengths of drilling fluid formulations

7.2 LPLT filtration tests and filter cake permeability analysis

Water based drilling fluid formulations are designed in such a way to maintain slightly higher hydrostatic pressure in the column of well bore compared to the formation pressure. During the drilling process of well bore, a part of drilling fluid invades to permeable formation of well bore and make a thin, low permeable filter cake on the wall of well bore. The solid components of drilling fluids deposited on the wall of well bore and prevent the further invasion of drilling fluid to the well bore formation. The use of bentonite only as drilling mud can cause many problems during drilling process due to the formation of thick permeable filter cake such as pipe sticking, high drag and torque is required, high pumping efficiency required. So, the addition of other filtrate loss additives such as polymer and nanoparticles help to make a thin and impermeable filter cake, less filtrate loss, minimum formation damage and borehole stability issues in the production zone.

Figure 7.5 presents the total fluid loss of drilling fluid formulation during the period of 30 minutes from low pressure and low temperature filter press apparatus. The base drilling fluid shows 19.4 ml filtrate volume while the addition of nanoparticles in the base drilling fluid slightly increase the filtrate volume from 19.4 ml to 20.6 ml for BT/N1 drilling fluid and from 19.4 ml to 22.8 ml for BT/N2 drilling fluid compared to the base drilling fluid. The increment of filtrate volume of by the addition of nanoparticles to the base has not significantly affected the filtrate volume. These results agree with the results of rheology of BT/N1 and BT/N2 drilling fluid formulations such as the addition of nanoparticles to the base drilling fluid affected the rheology of drilling fluid and in the equivalent way filtrate volume has increased slightly. The increase of filtrate volume by the addition of nanoparticles is due to the formation of small channels in the filter cake adjacent to the nanoparticles that increase the filtrate volume and related results were reported in literature [33]. The addition of polymer (P) to the base fluid has reduced the filtrate volume from 19.4 ml t0 10.7 ml only due to the adsorption of polymer with clay platelets and it was also considered as polymer makes thin layer of filter cake along with the presence of clay that further prevent the flow to drilling fluid through filter cake.

In the last, the incorporation of nanoparticles and polymer to the base drilling fluid has significantly reduced the filtrate volume of drilling fluids. The drilling fluid formulation BT/N1/P filtrate volume reduced from 19.4 ml to 8.6 ml and for BT/N2/P formulation filtrate volume reduced from 19.4 ml to 9 ml compared the base drilling fluid. It reduction of filtrate volume for the formulations of BT/N1/P and BT/N2/P results agree with the results of rheological properties such as plastic viscosity, apparent viscosity, gel strength and yield point. If the given formulation has high rheological properties, then the formulation of drilling fluid will produce less filtrate volume.

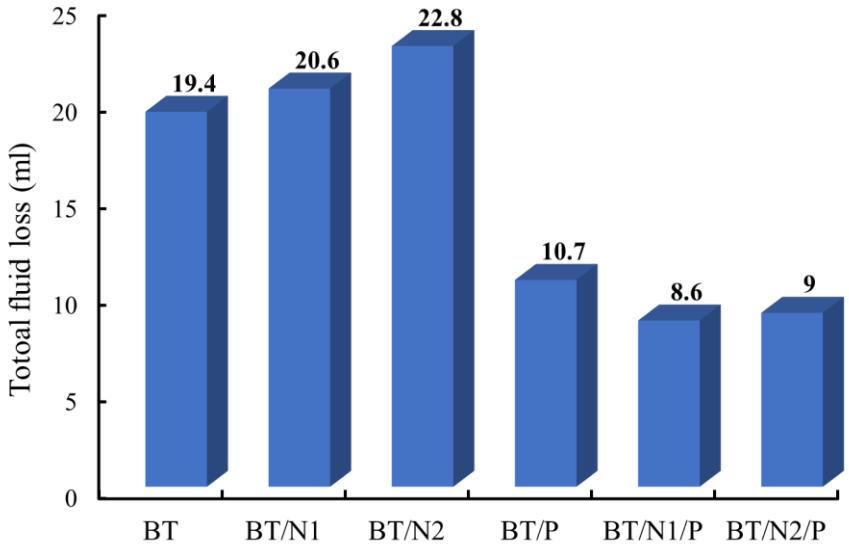

Figure 7.5 Total fluid loss of drilling fluid formulations

Figure 7.6 presents the filter cakes thickness corresponding to the different drilling fluid formulations. The base drilling fluid filter cake has 0.17 cm thickness while the addition of nanoparticles to the base drilling fluid has slightly increased the thickness of filter cake from 0.17 cm to 0.18 cm for BT/N1 drilling fluid and from 0.17 cm to 0.19 cm for BT/N2 drilling fluid. The addition of polymer to the base drilling fluid has significantly reduced the filter cake thickness from 0.17 cm to 0.13 cm thickness due to the compact structure of filter cake. The addition of nanoparticles and polymer to the base drilling fluid has reduced the filter cake thickness from 0.17 cm to 0.09 cm for BT/N1/P drilling fluid and from 0.17cm to 0.1 cm for BT/N2/P drilling fluid. The overall results show that the incorporation of polymer and nanoparticles to the base drilling fluid reduced the filter cake thickness and giving the compact structure filter cakes.

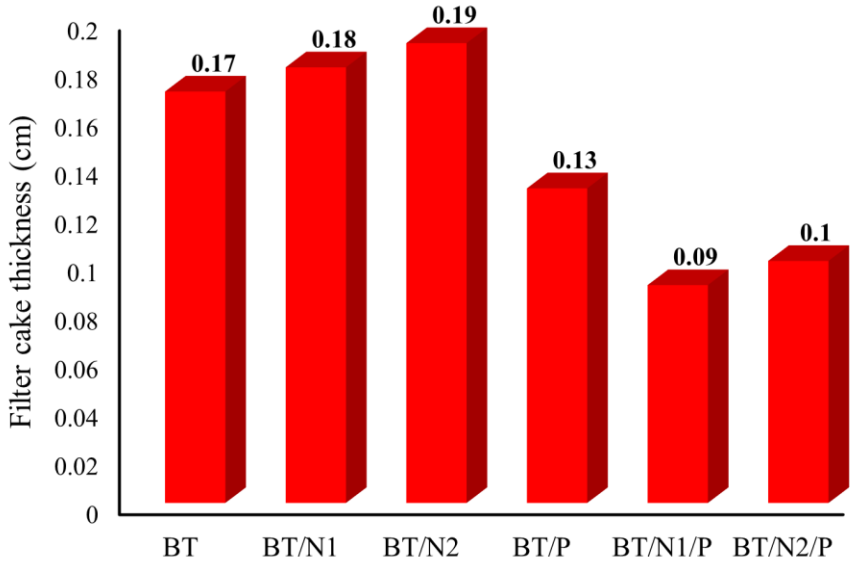

Figure 7.6 Filter cake thickness of drilling fluid formulations

Figure 7.7 presents the digital photographs of filter cake that were taken immediately after filtration experiment. After drying the filter cakes at room temperature, the thickness of filter cakes was measured using digital Vernier caliper and reported in centimeters. In Figure 7.8, the filtrate volume and square root of time shows the linear relationship. This linear relationship could be explained by Darcy's law for the measurement of filter cake permeabilities.

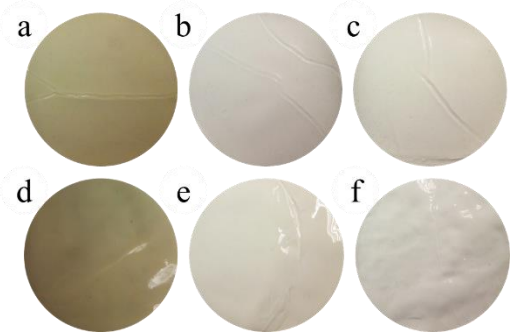

Figure 7.7 Digital photographs of filter cake samples obtained from LPLT filtration test. (a) BT, (b) BT/N1, (c) BT/N2, (d) BT/P, (e) BT/N1/P, (f) BT/N2/P

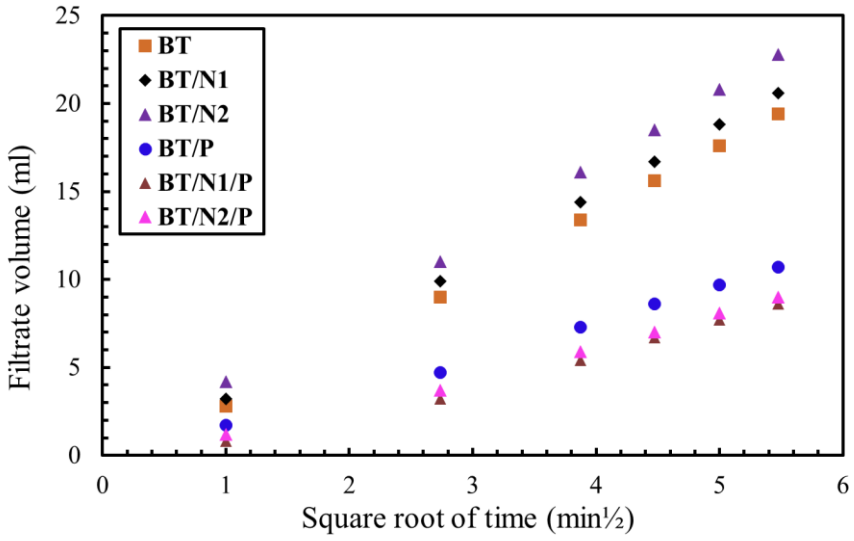

Figure 7.8 Filtrate volume vs square root of time for drilling fluid formulations under LPLT conditions

Table 7.1 presents the filter cake permeabilities corresponding to the six water based drilling fluid formulations. Darcy's law was used to measure the filter cake permeabilities for drilling fluids that pass through the filter medium. It was observed that base drilling fluid has 5.18 μD permeability and filter cake permeability is directly related to the filter cake thickness and filtrate volume. Higher the filter cake thickness and filtrate volume, then high would be the permeability of filter cakes. The addition of nanoparticles to the base drilling fluid has increase the permeability of BT/N1 (12.5%) and BT/N2 (31.4%) of drilling fluid filter cakes. This increased permeability is due to the reason which shows that nanoparticle and base fluid are not miscible with each other and the interface between nanoparticles and clay results the small channels in the filter cake that shows the increase in permeabilities [33]. The addition of polymer to the base drilling fluid has reduced the permeability (57.7%) of BT/P drilling fluid. The decrease in the value of permeability is due to less filtrate volume, decrease in the thickness of filter cake and compact structure of filter cake. The incorporation of polymer (P) and nanoparticles to the base drilling fluid has further reduced the permeabilities of filter

cake of BT/N1/P formulation by (76.6%) and BT/N2/P formulation by (66%) compared to the base drilling fluid. The overall results of permeability data show that the drilling fluid formulation containing polymer and nanoparticles in them produce the filter cake with minimum thickness, less filtrate volume, thin and impermeable filter cakes.

Table 7.1 Fluid loss, thickness and permeabilities of filter cakes of six drilling fluid formulations under LPLT condition

Formulations	Filtrate volume V_f (cm^3)	Filter cake thickness h_c (cm)	Permeability of filter cakes k (μD)	Ratio of permeability to thickness k/ h_c (μD/cm)
BT	19.4	0.17	5.18	30.51
BT/N1	20.6	0.18	5.83	32.38
BT/N2	22.8	0.19	6.81	35.84
BT/P	10.7	0.13	2.19	16.84
BT/N1/P	8.6	0.09	1.21	13.44
BT/N2/P	9	0.10	1.35	13.5

7.3 Filter cake SEM analysis

Figure 7.9 presents the scanning electron microscope images of six filter cake obtained after filtration experiments. The image (a) shows the filter cake of base drilling fluid in which the small pores and agglomerated clay particles can be seen that ultimately resulted 19.7 ml filtrate volume. The incorporation of nanoparticles in the base drilling fluid resulted two filter cakes such image (b) from BT/N1 formulation and image (c) from BT/N2 formulation. Both images show that open structure of filter cakes and agglomerated nanoparticles with clay platelets. The nanoparticles are immiscible with the components of base drilling fluid which creates the interface among the particles of BT/N1 and BT/N2 drilling fluid formulations. Due to the presence of interface among the particles, there are small channels through which liquid pass and results a high filtrate volume. The addition of polymer in image (d) to the base drilling fluid result a smooth filter cake in which clay particles and

polymer is homogeneously distributed. The polymer present in the base drilling fluid make a thin layer on the filter cake which prevent the passage of liquid through the filter cake. The incorporation of polymer and nanoparticles in the base drilling fluid results in reduced filtrate volume and permeability. The image (e) represent the BT/N1/P drilling fluid which shows that homogeneous distribution of nanoparticles in the filter cake. Here N1 represent TiO2 nanoparticles and these nanoparticles shows electrostatic repulsion among the particles at high pH values [90]. There is electrostatic repulsion among the polymer chains and nanoparticles (N1) which results the evenly distribution of nanoparticles in the image (e) filter cake. The image (f) represents the BT/N2/P drilling fluid filter cake. This filter shows the aggregation of polymer and clay platelets along with uneven distribution of nanoparticles in the filter cake which resulted the large crakes and channels in the filter and ultimately filtrate volume is slightly increased compared to the BT/N1/P drilling fluid formulation.

The overall results of SEM analysis show that BT/N1/P drilling fluid formulation shows maximum distribution of nanoparticles in the matrix of polymer and clay. This formulation also shows minimum filtrate volume and filter cake thickness. The SEM analysis also reveal that the presence of electrostatic repulsion among nanoparticles and nanoparticle with polymer chains would produce homogeneous dispersion of nanoparticles in filter cake.

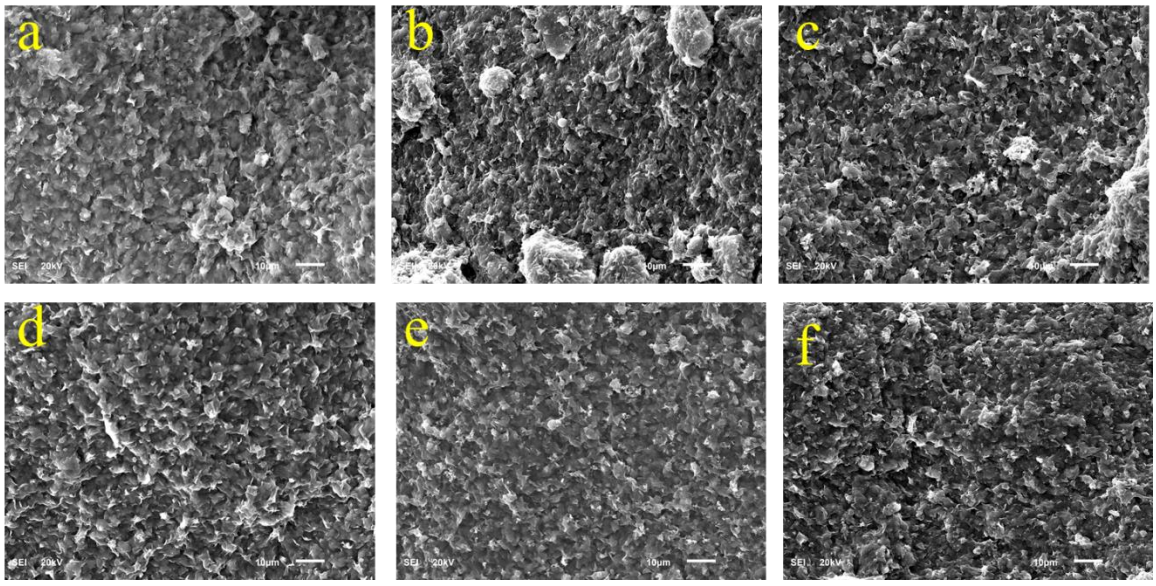

Figure 7.9 SEM images of filter cakes obtained from LPLT filtration test. (a) BT, (b) BT/N1, (c) BT/N2, (d) BT/P, (e) BT/N1/P, (f) BT/N2/P

CHAPTER 8

Conclusions and recommendations

8.1 Conclusions

The conclusion of each chapter is written as a separate paragraph to highlight the major findings and results.

Effect of electrolyte concentration and temperature on rheological properties of bentonite dispersions was investigated and experimental data were fitted to different rheological models including Cross model, Carreau model, Bingham model and Herschel-Bulkley model. The huge increases in yield stress, plastic viscosity and gel strength with the increase in bentonite concentration illustrate the three-dimensional edge-to-edge and edge-to-face association of bentonite particles. The decrease in flow index ‘n’ of Herschel-Bulkley model indicates the shear thinning behavior with an increase in bentonite concentration. While the increase in consistency index ‘k’ of viscosity models with an increase in concentration represents the onset of shear thinning at low shear rates. The presence of electrolyte strongly affects the associations among the bentonite particles and rheological parameters of Bingham and Herschel-Bulkley models. Yield stress, apparent viscosity, plastic viscosity and gel strength decrease with increase in electrolyte concentration. Bingham yield stress, Herschel-Bulkley yield stress, apparent viscosity, and gel strength decrease with the increase in the concentration of the electrolyte due to double layer compression and stronger face-to-face interactions among bentonite particles. High concentration of electrolyte produces enormous number of cations which accelerates the rate of flocculation among the platelets of bentonite. This flocculation is attributed to

the increased interactions of negatively charged silicate layers through the bridging of cations by diffusing the double layer structure. Hence, a further increase in temperature at fixed bentonite concentration in deionized water and salt water shows the improvement in rheological properties due to thermal induced swelling.

The rheological and filtration properties of bentonite/polymer dispersions were investigated using high molecular weight acrylamide-based copolymers. These polymers have a different degree of hydrolysis and different comonomers. The rheological experiments reveal that the polymer solution containing a higher degree of hydrolysis have better rheological properties compared to the polymer with a lesser degree of hydrolysis. The nature of comonomers is also important and the copolymer containing bulky comonomers (2-acrylamido-2-methylpropane sulfonic Acid) showed higher steady shear viscosity compared to the copolymer containing smaller comonomers (acrylic acid). The addition of high molecular weight into the bentonite dispersion significantly enhanced the rheological properties of bentonite. These rheological properties considerably depend on the nature and contents of comonomer of the acrylamide-based copolymer. Steady shear rheology data of bentonite and bentonite/polymer dispersions was obtained by fitting experimental data into Herschel-Bulkley model at 25°C and 85°C. The polymer containing acrylic acid showed the lowest viscosity in deionized water, however, when used in bentonite dispersion showed the highest viscosity. This suggests that the acrylamide-based copolymer containing smaller comonomers are a better choice over copolymers containing bulky comonomers. This behavior was consistent both at low and high temperatures. The yield stress of BT/ (polymer containing acrylic group) dispersion increased 1550% at 25°C and 1155% at 85°C compared to the bentonite dispersion. The flow behavior index ‘n’ at 25°C and 85°C was less than 1 indicating the non-Newtonian shear thinning behavior but the flow behavior index values at 85°C temperature are small compared to the 25°C depicting enhanced shear

thinning behavior at high temperature. The consistency coefficient 'K' is higher at an elevated temperature for all bentonite/polymer dispersions indicating the dependence of shear stress and viscosity on shear rate. The improved gel strength was observed for BT/ (polymer containing acrylic group) dispersion and increasing temperature increased the gel strength for all the dispersions. After aging the bentonite/polymer dispersions at 90°C, the rheological properties were enhanced but filtration properties were affected giving slightly higher fluid loss compared to the bentonite/polymer dispersions without aging. All added polymers improved the filtration properties significantly. However, they showed similar improvement and nature of comonomers and DOH has no major impact on filtration properties.

The rheological and filtration properties of Bent and Bent/polymer dispersions were examined using copolymer and terpolymer in deionized and salt water at 25°C and 85°C. These polymers contain two same monomers (AM and AMPS) but terpolymer has additional NVP monomer which contain five membered ring structure. The rheological properties of polymer solutions exhibit that terpolymer has better rheological properties in deionized and salt water at 25°C and 85°C compared to the copolymer. The superior properties of terpolymer were attributed to the presence of NVP monomer group in the backbone and offer additional interactions among the polymer chains which leads to higher rheological properties of the polymer solution. The rheological properties of Bent dispersion were significantly improved by the addition of polymers. The rheological properties of Bent/polymer dispersions mainly depend on the polymer structure, nature of monomers in the polymer chain, the chemical structure of monomer in the backbone, charge distribution in monomer groups and their distribution along the polymer chain. Out of all the Bent/polymer dispersions, BT/terpolymer dispersion in deionized water and BT/terpolymer/salt dispersion in salt water showed best rheological properties at 25°C and 85°C. The impressive results of BT/terpolymer and

BT/terpolymer/salt dispersions demonstrated that terpolymer polymer have better structural stability, have three distinct monomers including NVP which has ring structure and high charge distribution along the polymer chains compared to copolymer. All these distinctive features of terpolymer makes it suitable for one of the promising additive of water-based drilling fluids. The yield stress of BT/terpolymer and BT/copolymer dispersion was higher compared to the yield stress of Bent dispersion in deionized water. The presence of electrolyte considerably affects the yield stress of all Bent and Bent/polymer dispersions. The flow behavior index 'n' was less than 1 for all the Bent and Bent/polymer dispersions at 25°C and 85°C illustrating the non-Newtonian behavior. The enhanced gel strength of BT/terpolymer and BT/terpolymer/salt dispersions in deionized and salt water also supported the results of steady shear rheology. The addition of polymers in Bent dispersion results in the decrease in filtrate volume. The presence of an electrolyte (salt) results in the slight increase in filtrate volume of Bent/polymer dispersions. The filtration experiments showed that Bent/terpolymer dispersion has minimum filtrate volume compared to the other Bent and Bent/polymer dispersion in deionized and salt water. Hence, the terpolymer polymer would be a suitable candidate for water-based drilling fluids due to its enhanced rheological properties with minimum filtrate volume.

The rheological properties such as apparent viscosity, plastic viscosity, yield point, and gel strengths were measured for six water base drilling fluid formulations. The polymer used in the drilling fluid formulation has hydrophilic and hydrophobic moieties in its structure which interacts with other drilling fluid additives such as bentonite and nanoparticles to enhance the rheological properties. The incorporation of nanoparticles in the base drilling fluid has no significant impact on rheological properties. But the addition of polymer in the base fluid significantly increased the rheological properties of base drilling fluid. The combined addition of polymer and nanoparticles has noticeable

increase in rheological properties. Among all the six drilling fluid formulations, BT/N1/P formulation shows maximum rheological properties. The filtration properties of six drilling fluid formulation shows that addition of nanoparticles in the base drilling fluid increased the filtrate volume, filter cake thickness and permeability due to the improper distribution of nanoparticles and formation of channels adjacent to interface of clay and nanoparticles. The incorporation of polymer in the base drilling fluid has significantly reduced the filtrate volume, filter cake thickness and permeability due to the adsorption of polymer on clay platelets which forms a thin layer on filter cake and reduced the filtrate volume with compact filter cake structure. The combined addition of polymer and nanoparticles in the base drilling fluid has maximum reduction in filtrate volume, thickness of filter cake and reduced permeability. This is due to the even distribution of nanoparticles in clay and polymer matrix on the filter cake. The electrostatic repulsion among the nanoparticles and polymer chains also help for the distribution of nanoparticles. Among all the formulations, BT/N1/P shows superior filtration characteristics such as 54% reduction in filtrate volume, 47% reduction in filter cake thickness and 76.6% reduction in permeability compared to the base drilling fluid. The SEM analysis also shows that BT/N1/P drilling fluid filter cake has maximum distribution of nanoparticles in clay and polymer matrix.

8.2 Recommendations

The use of nanoparticles in the drilling fluid formulation results in the form of aggregation. To avoid this problem, the surface modified nanoparticles could be used to improve the dispersion stability of drilling fluid formulations.

References

[1] A. Aftab, A. Ismail, S. Khokhar, Z.H. Ibupoto, Novel zinc oxide nanoparticles deposited acrylamide composite used for enhancing the performance of water-based drilling fluids at elevated temperature conditions, Journal of Petroleum Science and Engineering, 146 (2016) 1142-1157.

[2] R. Caenn, G.V. Chillingar, Drilling fluids: State of the art, journal of petroleum science and engineering, 14 (1996) 221-230.

[3] K. Fattah, A. Lashin, Investigation of mud density and weighting materials effect on drilling fluid filter cake properties and formation damage, Journal of African Earth Sciences, 117 (2016) 345-357.

[4] S. Boussen, D. Sghaier, F. Chaabani, B. Jamoussi, S.B. Messaoud, A. Bennour, The rheological, mineralogical and chemical characteristic of the original and the Na 2 CO 3-activated Tunisian swelling clay (Aleg Formation) and their utilization as drilling mud, Applied Clay Science, 118 (2015) 344-353.

[5] M. Sadeghalvaad, S. Sabbaghi, The effect of the TiO2/polyacrylamide nanocomposite on water-based drilling fluid properties, Powder Technology, 272 (2015) 113-119.

[6] A.S. Ragab, A. Noah, Reduction of formation damage and fluid loss using nano-sized silica drilling fluids, Petroleum Technology Development Journal, 2 (2014) 75-88.

[7] J.K.M. William, S. Ponmani, R. Samuel, R. Nagarajan, J.S. Sangwai, Effect of CuO and ZnO nanofluids in xanthan gum on thermal, electrical and high pressure rheology of water-based drilling fluids, Journal of Petroleum Science and Engineering, 117 (2014) 15-27.

[8] S. Sadegh Hassani, A. Amrollahi, A. Rashidi, M. Soleymani, S. Rayatdoost, The effect of nanoparticles on the heat transfer properties of drilling fluids, Journal of Petroleum Science and Engineering, 146 (2016) 183-190.

[9] H.H. Murray, Bentonite applications, Developments in Clay Science, 2 (2006) 111-130.

[10] B. Abu-Jdayil, Rheology of sodium and calcium bentonite–water dispersions: Effect of electrolytes and aging time, International journal of mineral processing, 98 (2011) 208-213.

[11] V. Kelessidis, R. Maglione, Yield stress of water–bentonite dispersions, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 318 (2008) 217-226.

[12] J.T. Shakib, V. Kanani, P. Pourafshary, Nano-clays as additives for controlling filtration properties of water–bentonite suspensions, Journal of Petroleum Science and Engineering, 138 (2016) 257-264.

[13] S. Mishra, Effect of different bonding agents on sintering behaviour of al2o3-sio2 based mortar, 2014.

[14] A. Aftab, A. Ismail, Z. Ibupoto, Enhancing the rheological properties and shale inhibition behavior of water-based mud using nanosilica, multi-walled carbon nanotube, and graphene nanoplatelet, Egyptian Journal of Petroleum, DOI (2016).

[15] M.A. Agha, R.E. Ferrell, G.F. Hart, M.S.A. El Ghar, A. Abdel-Motelib, Physical properties and Na-activation of Egyptian bentonitic clays for appraisal of industrial applications, Applied Clay Science, 131 (2016) 74-83.

[16] S. Shirazi, S. Wiwat, H. Kazama, J. Kuwano, M. Shaaban, Salinity effect on swelling characteristics of compacted bentonite, Environment Protection Engineering, 37 (2011) 65-74.

[17] E. Santoyo, S. Santoyo-Gutierrez, A. García, G. Espinosa, S. Moya, Rheological property measurement of drilling fluids used in geothermal wells, Applied Thermal Engineering, 21 (2001) 283-302.

[18] Y. Wu, Z. Wang, Z. Yan, T. Zhang, Y. Bai, P. Wang, P. Luo, S. Gou, Q. Guo, Poly (2-acrylamide-2-methylpropanesulfonic acid)-Modified SiO2 Nanoparticles for Water-Based Muds, Industrial & Engineering Chemistry Research, 56 (2016) 168-174.

[19] V.C. Kelessidis, C. Tsamantaki, A. Michalakis, G.E. Christidis, P. Makri, K. Papanicolaou, A. Foscolos, Greek lignites as additives for controlling filtration properties of water–bentonite suspensions at high temperatures, Fuel, 86 (2007) 1112-1121.

[20] A.R. Ismail, N.M. Rashid, M.Z. Jaafar, W.R.W. Sulaiman, N.A. Buang, Effect of nanomaterial on the rheology of drilling fluids, Journal of Applied Sciences, 14 (2014) 1192.

[21] N. Yildiz, Y. Sarikaya, A. Calimli, The effect of the electrolyte concentration and pH on the rheological properties of the original and the Na 2 CO 3-activated Kütahya bentonite, Applied Clay Science, 14 (1999) 319-327.

[22] K.Y. Choo, K. Bai, Effects of bentonite concentration and solution pH on the rheological properties and long-term stabilities of bentonite suspensions, Applied Clay Science, 108 (2015) 182-190.

[23] Z. Luo, J. Pei, L. Wang, P. Yu, Z. Chen, Influence of an ionic liquid on rheological and filtration properties of water-based drilling fluids at high temperatures, Applied Clay Science, 136 (2017) 96-102.

[24] M. Khodja, J.P. Canselier, F. Bergaya, K. Fourar, M. Khodja, N. Cohaut, A. Benmounah, Shale problems and water-based drilling fluid optimisation in the Hassi Messaoud Algerian oil field, Applied Clay Science, 49 (2010) 383-393.

[25] N. Alderman, A. Gavignet, D. Guillot, G. Maitland, High-temperature, high-pressure rheology of water-based muds, SPE Annual Technical Conference and Exhibition, Society of Petroleum Engineers, 1988.

[26] W. Li, X. Zhao, H. Peng, J. Guo, T. Ji, B. Chen, Z. You, L. Liu, A Novel Environmentally Friendly Lubricant for Water-Based Drilling Fluids as a New Application of Biodiesel, IADC/SPE Asia Pacific Drilling Technology Conference, Society of Petroleum Engineers, 2016.

[27] F. Makinde, A. Adejum, C. Ako, V.E. Efeovbokhan, Modelling the effects of temperature and aging time on the rheological properties of drilling fluids, Petroleum & Coal, 53 (2011) 167-182.

[28] Y. Lin, L.K.-J. Cheah, N. Phan-Thien, B.C. Khoo, Effect of temperature on rheological behavior of kaolinite and bentonite suspensions, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 506 (2016) 1-5.

[29] A.K. Garakani, N. Mostoufi, F. Sadeghi, H. Fatourechi, M. Sarrafzadeh, M. Mehrnia, Comparison between different models for rheological characterization of activated sludge, Journal of Environmental Health Science & Engineering, 8 (2011) 255-264.

[30] W. Huang, Y.-K. Leong, T. Chen, P.-I. Au, X. Liu, Z. Qiu, Surface chemistry and rheological properties of API bentonite drilling fluid: pH effect, yield stress, zeta potential and ageing behaviour, Journal of Petroleum Science and Engineering, 146 (2016) 561-569.

[31] M.-C. Li, Q. Wu, K. Song, Y. Qing, Y. Wu, Cellulose nanoparticles as modifiers for rheology and fluid loss in bentonite water-based fluids, ACS applied materials & interfaces, 7 (2015) 5006-5016.

[32] S. Rossi, P. Luckham, S. Zhu, B. Briscoe, T.F. Tadros, Influence of low molecular weight polymers on the rheology of bentonite suspensions, Revue de l'institut Français du pétrole, 52 (1997) 199-206.

[33] H. Zhong, Z. Qiu, Z. Tang, X. Zhang, J. Xu, W. Huang, Study of 4, 4′-methylenebis-cyclohexanamine as a high temperature-resistant shale inhibitor, Journal of Materials Science, 51 (2016) 7585-7597.

[34] K. Song, Q. Wu, M.-C. Li, A.K. Wojtanowicz, L. Dong, X. Zhang, S. Ren, T. Lei, Performance of low solid bentonite drilling fluids modified by cellulose nanoparticles, Journal of Natural Gas Science and Engineering, 34 (2016) 1403-1411.

[35] S.I. Reilly, Z. Vryzas, V.C. Kelessidis, D. Gerogiorgis, First-principles rheological modelling and parameter estimation for nanoparticle-based smart drilling fluids, Comput. Aided Chem. Eng, 38 (2016) 1039-1044.

[36] N. Wahid, M.A.M. Yusof, N.H. Hanafi, Optimum Nanosilica Concentration in Synthetic Based Mud (SBM) for High Temperature High Pressure Well, SPE/IATMI Asia Pacific Oil & Gas Conference and Exhibition, Society of Petroleum Engineers, 2015.

[37] V. Mahto, V.P. Sharma, Rheological study of a water based oil well drilling fluid, Journal of Petroleum Science and Engineering, 45 (2004) 123-128.

[38] L.-M. Zhang, Y.-B. Tan, Z.-M. Li, Application of a new family of amphoteric cellulose-based graft copolymers as drilling-mud additives, Colloid & Polymer Science, 277 (1999) 1001-1004.

[39] A. Aftab, A.R. Ismail, Z.H. Ibupoto, H. Akeiber, M.G.K. Malghani, Nanoparticles based drilling muds a solution to drill elevated temperature wells: A review, Renewable and Sustainable Energy Reviews, 76 (2017) 1301-1313.

[40] G.T. Teixeira, R.F.T. Lomba, S.A. Fontoura, V.A. Melendez, E. Ribeiro, A.D. Francisco, R.S. Nascimento, New Material for Wellbore Strengthening and Fluid Losses Mitigation in Deepwater Drilling Scenario, SPE Deepwater Drilling and Completions Conference, Society of Petroleum Engineers, 2014.

[41] M.C. Li, Q. Wu, K. Song, S. Lee, C. Jin, S. Ren, T. Lei, Soy Protein Isolate As Fluid Loss Additive in Bentonite-Water-Based Drilling Fluids, ACS applied materials & interfaces, 7 (2015) 24799-24809.

[42] A. Aftab, A.R. Ismail, S. Khokhar, Z.H. Ibupoto, Novel zinc oxide nanoparticles deposited acrylamide composite used for enhancing the performance of water-based drilling fluids at elevated temperature conditions, Journal of Petroleum Science and Engineering, 146 (2016) 1142-1157.

[43] P. Allahvirdizadeh, E. Kuru, M. Parlaktuna, Experimental investigation of solids transport in horizontal concentric annuli using water and drag reducing polymer-based fluids, Journal of Natural Gas Science and Engineering, 35 (2016) 1070-1078.

[44] S. Kafashi, M. Rasaei, G. Karimi, Effects of sugarcane and polyanionic cellulose on rheological properties of drilling mud: An experimental approach, Egyptian journal of petroleum, 26 (2017) 371-374.

[45] C. Guo, L. Zhou, J. Lv, Effects of expandable graphite and modified ammonium polyphosphate on the flame-retardant and mechanical properties of wood flour-polypropylene composites, Polymers & Polymer Composites, 21 (2013) 449.

[46] R. Jain, V. Mahto, V.P. Sharma, Evaluation of polyacrylamide-grafted-polyethylene glycol/silica nanocomposite as potential additive in water based drilling mud for reactive shale formation, Journal of Natural Gas Science and Engineering, 26 (2015) 526-537.

[47] M. Lal, Shale stability: drilling fluid interaction and shale strength, SPE Asia Pacific Oil and Gas Conference and Exhibition, Society of Petroleum Engineers, 1999.

[48] X. Ma, Z. Zhu, W. Shi, Y. Hu, Synthesis and application of a novel betaine-type copolymer as fluid loss additive for water-based drilling fluid, Colloid and Polymer Science, 295 (2016) 53-66.

[49] P.J. Boul, B. Reddy, J. Zhang, C. Thaemlitz, Functionalized Nanosilicas as Shale Inhibitors in Water-Based Drilling Fluids, SPE Drilling & Completion, DOI (2017).

[50] R. Jain, B.K. Paswan, T.K. Mahto, V. Mahto, Study the effect of synthesized graft copolymer on the inhibitive water based drilling fluid system, Egyptian Journal of Petroleum, DOI 10.1016/j.ejpe.2015.03.016(2015).

[51] S. Baba Hamed, M. Belhadri, Rheological properties of biopolymers drilling fluids, Journal of Petroleum Science and Engineering, 67 (2009) 84-90.

[52] R. Jain, T.K. Mahto, V. Mahto, Rheological investigations of water based drilling fluid system developed using synthesized nanocomposite, Korea-Australia Rheology Journal, 28 (2016) 55-65.

[53] R. Sengupta, S. Chakraborty, S. Bandyopadhyay, S. Dasgupta, R. Mukhopadhyay, K. Auddy, A. Deuri, A short review on rubber/clay nanocomposites with emphasis on mechanical properties, Polymer Engineering & Science, 47 (2007) 1956-1974.

[54] L.M. Gouveia, B. Grassl, A.J. Muller, Synthesis and rheological properties of hydrophobically modified polyacrylamides with lateral chains of poly(propylene oxide) oligomers, Journal of colloid and interface science, 333 (2009) 152-163.

[55] E. Volpert, J. Selb, F. Candau, Associating behaviour of polyacrylamides hydrophobically modified with dihexylacrylamide, Polymer, 39 (1998) 1025-1033.

[56] K. Song, Q. Wu, M. Li, S. Ren, L. Dong, X. Zhang, T. Lei, Y. Kojima, Water-based bentonite drilling fluids modified by novel biopolymer for minimizing fluid loss and formation damage, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 507 (2016) 58-66.

[57] A.G. Iscan, M.V. Kok, Effects of Polymers and CMC Concentration on Rheological and Fluid Loss Parameters of Water-Based Drilling Fluids, Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 29 (2007) 939-949.

[58] J. Abdo, M.D. Haneef, Clay nanoparticles modified drilling fluids for drilling of deep hydrocarbon wells, Applied Clay Science, 86 (2013) 76-82.

[59] A. Aftab, A.R. Ismail, Z.H. Ibupoto, Enhancing the rheological properties and shale inhibition behavior of water-based mud using nanosilica, multi-walled carbon nanotube, and graphene nanoplatelet, Egyptian Journal of Petroleum, 26 (2017) 291-299.

[60] M.-C. Li, Q. Wu, K. Song, S. Lee, C. Jin, S. Ren, T. Lei, Soy protein isolate as fluid loss additive in bentonite–water-based drilling fluids, ACS applied materials & interfaces, 7 (2015) 24799-24809.

[61] N.S. Al-Zubaidi, A.A. Alwasiti, D. Mahmood, A comparison of nano bentonite and some nano chemical additives to improve drilling fluid using local clay and commercial bentonites, Egyptian Journal of Petroleum, DOI (2016).

[62] J. Abdo, R. Zaier, E. Hassan, H. AL-Sharji, A. Al-Shabibi, ZnO–clay nanocomposites for enhance drilling at HTHP conditions, Surface and Interface Analysis, 46 (2014) 970-974.

[63] R. Jain, V. Mahto, V. Sharma, Evaluation of polyacrylamide-grafted-polyethylene glycol/silica nanocomposite as potential additive in water based drilling mud for reactive shale formation, Journal of Natural Gas Science and Engineering, 26 (2015) 526-537.

[64] X. Ma, Z. Zhu, W. Shi, Y. Hu, Synthesis and application of a novel betaine-type copolymer as fluid loss additive for water-based drilling fluid, Colloid and Polymer Science, 295 (2017) 53-66.

[65] P.F. Luckham, S. Rossi, The colloidal and rheological properties of bentonite suspensions, Advances in colloid and interface science, 82 (1999) 43-92.

[66] O. M'bodj, N.K. Ariguib, M.T. Ayadi, A. Magnin, Plastic and elastic properties of the systems interstratified clay–water–electrolyte–xanthan, Journal of colloid and interface science, 273 (2004) 675-684.

[67] V.C. Kelessidis, M. Zografou, V. Chatzistamou, Optimization of drilling fluid rheological and fluid loss properties utilizing PHPA polymer, SPE Middle East Oil and Gas Show and Conference, Society of Petroleum Engineers, 2013.

[68] A. Benchabane, K. Bekkour, Effects of anionic additives on the rheological behavior of aqueous calcium montmorillonite suspensions, Rheologica Acta, 45 (2006) 425-434.

[69] D. Zhao, H. Liu, W. Guo, L. Qu, C. Li, Effect of inorganic cations on the rheological properties of polyacrylamide/xanthan gum solution, Journal of Natural Gas Science and Engineering, 31 (2016) 283-292.

[70] M.G. Temraz, I. Hassanien, Mineralogy and rheological properties of some Egyptian bentonite for drilling fluids, Journal of Natural Gas Science and Engineering, 31 (2016) 791-799.

[71] M.S. Kamal, A.S. Sultan, U.A. Al-Mubaiyedh, I.A. Hussein, Review on polymer flooding: rheology, adsorption, stability, and field applications of various polymer systems, Polymer Reviews, 55 (2015) 491-530.

[72] R. Jain, V. Mahto, Evaluation of polyacrylamide/clay composite as a potential drilling fluid additive in inhibitive water based drilling fluid system, Journal of Petroleum Science and Engineering, 133 (2015) 612-621.

[73] R. Jain, V. Mahto, Formulation of a water based drilling fluid system with synthesized graft copolymer for troublesome shale formations, Journal of Natural Gas Science and Engineering, 38 (2017) 171-181.

[74] T.W. Beihoffer, D.S. Dorrough, D.D. Schmidt, The Development of an Inhibitive Cationic Drilling Fluid for Slim-Hole Coring Applications, Society of Petroleum Engineers.

[75] D.S. Ibrahim, N.A. Sami, N. Balasubramanian, Effect of barite and gas oil drilling fluid additives on the reservoir rock characteristics, Journal of Petroleum Exploration and Production Technology, 7 (2016) 281-292.

[76] M.M. Jalili, K. Davoudi, E. Zafarmand Sedigh, S. Farrokhpay, Surface treatment of TiO2 nanoparticles to improve dispersion in non-polar solvents, Advanced Powder Technology, 27 (2016) 2168-2174.

[77] H. Mao, Z. Qiu, Z. Shen, W. Huang, Hydrophobic associated polymer based silica nanoparticles composite with core–shell structure as a filtrate reducer for drilling fluid at utra-high temperature, Journal of Petroleum Science and Engineering, 129 (2015) 1-14.

[78] H. Pham, Q.P. Nguyen, Effect of silica nanoparticles on clay swelling and aqueous stability of nanoparticle dispersions, Journal of nanoparticle research : an interdisciplinary forum for nanoscale science and technology, 16 (2014) 2137.

[79] C.Y. Wu, K.J. Tu, J.P. Deng, Y.S. Lo, C.H. Wu, Markedly Enhanced Surface Hydroxyl Groups of TiO(2) Nanoparticles with Superior Water-Dispersibility for Photocatalysis, Materials, 10 (2017).

[80] M.C. Li, Q. Wu, K. Song, Y. Qing, Y. Wu, Cellulose nanoparticles as modifiers for rheology and fluid loss in bentonite water-based fluids, ACS applied materials & interfaces, 7 (2015) 5006-5016.

[81] M.-C. Li, C. Mei, X. Xu, S. Lee, Q. Wu, Cationic surface modification of cellulose nanocrystals: Toward tailoring dispersion and interface in carboxymethyl cellulose films, Polymer, 107 (2016) 200-210.

[82] Y. Liu, K. Gordeyeva, L. Bergström, Steady-shear and viscoelastic properties of cellulose nanofibril–nanoclay dispersions, Cellulose, 24 (2017) 1815-1824.

[83] F. Yang, G. Li, Y.-G. He, F.-X. Ren, G.-x. Wang, Synthesis, characterization, and applied properties of carboxymethyl cellulose and polyacrylamide graft copolymer, Carbohydrate polymers, 78 (2009) 95-99.

[84] R. Anderson, I. Ratcliffe, H. Greenwell, P. Williams, S. Cliffe, P. Coveney, Clay swelling—a challenge in the oilfield, Earth-Science Reviews, 98 (2010) 201-216.

[85] P.J. Boul, B. Reddy, M. Hillfiger, T.P. O'Connell, Functionalized Nanosilicas as Shale Inhibitors in Water-Based Drilling Fluids, Offshore Technology Conference, Offshore Technology Conference, 2016.

[86] D. Penner, G. Lagaly, Influence of anions on the rheological properties of clay mineral dispersions, Applied Clay Science, 19 (2001) 131-142.

[87] X. Zhang, G. Jiang, Y. Xuan, L. Wang, X. Huang, The Development of a Viscosifier for Clay Free and Water Based Drilling Fluid With High Density and High Temperature Resistant, IADC/SPE Asia Pacific Drilling Technology Conference, Society of Petroleum Engineers, 2016.

[88] N.M. Taha, S. Lee, Nano Graphene Application Improving Drilling Fluids Performance, International Petroleum Technology Conference, International Petroleum Technology Conference, 2015.

[89] D.V. Kosynkin, G. Ceriotti, K.C. Wilson, J.R. Lomeda, J.T. Scorsone, A.D. Patel, J.E. Friedheim, J.M. Tour, Graphene oxide as a high-performance fluid-loss-control additive in water-based drilling fluids, ACS applied materials & interfaces, 4 (2011) 222-227.

[90] M. Abdou, A. Al-Sabagh, M. Dardir, Evaluation of Egyptian bentonite and nano-bentonite as drilling mud, Egyptian Journal of Petroleum, 22 (2013) 53-59.

[91] S.B. Hamed, M. Belhadri, Rheological properties of biopolymers drilling fluids, Journal of Petroleum Science and Engineering, 67 (2009) 84-90.

[92] P.-I. Au, Y.-K. Leong, Rheological and zeta potential behaviour of kaolin and bentonite composite slurries, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 436 (2013) 530-541.

[93] C. Anyanwu, M. Mustapha Unubi, Experimental Evaluation of Particle Sizing in Drilling Fluid to Minimize Filtrate Losses and Formation Damage, SPE Nigeria Annual International Conference and Exhibition, Society of Petroleum Engineers, 2016.

[94] A. Babajide, O. Adebowale, F. Adesina, A. Churchill, M. Ifechukwu, Effects of Temperature and Pressure on Shale Cuttings Dispersion in Water Based Mud WBM Using NACL, CACL2, KCL Salts as Primary Inhibiting Agents and Polymer XCD Xanthan Gum as Secondary Inhibiting Agent, SPE Nigeria Annual International Conference and Exhibition, Society of Petroleum Engineers, 2016.

[95] S.N. Shah, N.H. Shanker, C.C. Ogugbue, Future challenges of drilling fluids and their rheological measurements, AADE fluids conference and exhibition, Houston, Texas, 2010.

[96] T. Cortner, E. Trickey, Predicting Toxicity for Simple Water-Based Drilling Fluids Using a Response Surface Methodology, SPE International Conference and Exhibition on Health, Safety, Security, Environment, and Social Responsibility, Society of Petroleum Engineers, 2016.

[97] A. Benslimane, I.M. Bahlouli, K. Bekkour, D. Hammiche, Thermal gelation properties of carboxymethyl cellulose and bentonite-carboxymethyl cellulose dispersions: Rheological considerations, Applied Clay Science, 132-133 (2016) 702-710.

[98] M. Sadeghalvaad, S. Sabbaghi, The effect of the TiO 2/polyacrylamide nanocomposite on water-based drilling fluid properties, Powder Technology, 272 (2015) 113-119.

[99] V. Mahto, V. Sharma, Rheological study of a water based oil well drilling fluid, Journal of Petroleum Science and Engineering, 45 (2004) 123-128.

[100] S.S. Hassani, A. Amrollahi, A. Rashidi, M. Soleymani, S. Rayatdoost, The effect of nanoparticles on the heat transfer properties of drilling fluids, Journal of Petroleum Science and Engineering, 146 (2016) 183-190.

[101] V. Kelessidis, R. Maglione, C. Tsamantaki, Y. Aspirtakis, Optimal determination of rheological parameters for Herschel–Bulkley drilling fluids and impact on pressure drop, velocity profiles and penetration rates during drilling, Journal of Petroleum Science and Engineering, 53 (2006) 203-224.

[102] V. Kelessidis, R. Maglione, Modeling rheological behavior of bentonite suspensions as Casson and Robertson–Stiff fluids using Newtonian and true shear rates in Couette viscometry, Powder technology, 168 (2006) 134-147.

[103] X. Meng, Y. Zhang, F. Zhou, P.K. Chu, Effects of carbon ash on rheological properties of water-based drilling fluids, Journal of Petroleum Science and Engineering, 100 (2012) 1-8.

[104] R. Rooki, F.D. Ardejani, A. Moradzadeh, H. Mirzaei, V. Kelessidis, R. Maglione, M. Norouzi, Optimal determination of rheological parameters for herschel-bulkley drilling fluids using genetic algorithms (GAs), Korea-Australia Rheology Journal, 24 (2012) 163-170.

[105] M.M. Barry, Y. Jung, J.-K. Lee, T.X. Phuoc, M.K. Chyu, Fluid filtration and rheological properties of nanoparticle additive and intercalated clay hybrid bentonite drilling fluids, Journal of Petroleum Science and Engineering, 127 (2015) 338-346.

[106] A.K. Garakani, N. Mostoufi, F. Sadeghi, M. Hosseinzadeh, H. Fatourechi, M. Sarrafzadeh, M. Mehrnia, Comparison between different models for rheological characterization of activated sludge, Iranian journal of environmental health science & engineering, 8 (2011) 255.

[107] V.C. Kelessidis, C. Papanicolaou, A. Foscolos, Application of Greek lignite as an additive for controlling rheological and filtration properties of water–bentonite suspensions at high temperatures: A review, International Journal of Coal Geology, 77 (2009) 394-400.

[108] F. Galindo-Rosales, F. Rubio-Hernández, Structural breakdown and build-up in bentonite dispersions, Applied Clay Science, 33 (2006) 109-115.

Vitae

Name :Hafiz Mudaser Ahmad

Nationality :Pakistani

Date of Birth :8/27/1990

Phone :(0092-3334978514), (00966-595242951)

Email :(g201408780@kfupm.edu.sa), (hafiz.mudassir89@hotmail.com)

Address :House No. 1A-3 Street No. 21 Dev Samaj Road Sanat Nagar Lahore (56131), Pakistan

Research Interests

Complex Fluid Properties
Inhabitation of shale swelling
Colloids and Dispersions Rheology
Clay Polymer Nanocomposites
Synthesis of Polymer Nanocomposites
Surfactants and Ionic liquid-based fluids

Education

M.Sc., Chemical Engineering, 2015-2017
King Fahd University of Petroleum & Minerals at Dhahran, Saudi Arabia
Thesis: Enhancing water based drilling fluid performance using polymers and nanoparticles

B.Sc., Chemical (Polymer) Engineering, 2009-2014
University of Engineering & Technology, Lahore, Pakistan
Thesis: Amine sweetening and dehydration of natural gas

MS Thesis Work

I worked on master's research topic named as "Enhancing water based drilling fluid performance using polymers and nanoparticles". The research includes the following responsibilities

- Identification of loopholes in drilling fluids operations
- Extensive literature review
- Selection of novel materials for drilling fluids
- Synthesis and preparation of drilling fluids
- Evaluation and measurement of drilling fluid properties
- Analysis of results obtained from experiments
- Presentation of results to advisory committee

BS Projects

- Plant design final year project of "Amine sweetening and dehydration of natural gas"
- Fabrication of nanocomposite (glass fiber/Vinyl ester with nanosilica) to enhance fiber matrix interaction and make the composite with high mechanical and thermal properties.
- Conductive Blends of Polyaniline with Thermoplastics by emulsion polymerization and its characterization
- Preparation of polypropylene (PP) and SBR rubber blend and its characterization
- Participated as a team leader with four engineering students to research and design projects. Coordinated team presentation to faculty of department
- Created business plan and prospectus as team leader in Entrepreneurship class project

Industrial Experience

- Four weeks internship experience (unpaid) at AGRI TECH
  Pak American Fertilizer, Mianwali, 2012
- Quality control Engineer at Crystallite Plastics, Lahore
  Two-month unpaid training (November-December), 2014

Teaching and Administrative Work Experience

- Worked as teaching assistant and grader for Chemical Engineering Thermodynamics, Petroleum Refining and Petrochemical Industries at KFUPM
- Served as assistant at deanship of graduate studies for undergraduate and graduate students to assist registration and course selection process at KFUPM
- Worked as graduate assistant for teaching fluid mechanics lab at undergraduate level, KFUPM

Technical and Other Skills

- Proficient in modeling of drilling fluid properties which include rheological, filtration and shale inhibition
- Persuasive communication skills oral, written, and presentation
- Software: Microsoft Office, Mathematica, Mat Lab
- Spoken Languages: Fluent in English, Urdu, and learning Arabic
- Hobbies: Playing cricket and Badminton, reading books

Accomplishments/Certificates

- Obtained Fully Funded Scholarship for graduate studies at KFUPM
- Obtained 2nd position in University Student Forum conference at KFUPM
- Obtained certificate of Achievement from University Student Forum Conference at KFUPM
- Obtained certificate of recognition and technical paper presentation at the 2017 SPE-KSA Annual Technical Symposium & Exhibition (ATS&E)
- Obtained internship certificate remarked as excellent performance.
- Obtained Dean's Honor roll in third and sixth semester in Graduation

Research Equipment Used

- Discovery Hybrid Rheometer
- Anton-Paar High Pressure /Temperature Rheometer
- Core Flooding System
- Low Pressure/Low Temperature Filtration Apparatus
- High Pressure/High Temperature Filtration Apparatus
- Fann Low Temperature/High Temperature Viscometers
- Fourier transform infrared spectroscopy (FTIR)
- Thermal gravimetric analysis (TGA)
- Scanning Electron Microscope (SEM)
- Linear swell Meter
- Zeta Potential Analyzer

Publications

Journal Publications

1. Hafiz Mudaser Ahmad, Muhammad Shahzad Kamal, Mamdouh Al-Harthi "***High Molecular Weight Copolymers as Rheology Modifier and Fluid Loss Additive for Water-based Drilling Fluids***". Journal of Molecular Liquids. 2017, 252, 133-143. doi.org/10.1016/j.molliq.2017. 12.135
2. Hafiz Mudaser Ahmad, Muhammad Shahzad Kamal, Mamdouh Al-Harthi "***Rheological and Filtration Properties of Clay-Polymer Systems: Impact of Polymer Structure***" Applied Clay Science. 2018, https://doi.org/10.1016/j.clay.2018.01.016

3. Hafiz Mudaser Ahmad, Muhammad Shahzad Kamal, Mamdouh Al-Harthi "***Effect of thermal aging and electrolyte on bentonite dispersions: Rheology and morphological properties***" (Submitted to Colloids and Surfaces A: Physicochemical and Engineering Aspects)
4. Hafiz Mudaser Ahmad, Muhammad Shahzad Kamal, Mamdouh Al-Harthi "***Enhancing wellbore stability and drilling fluid performance using associative polymer and TiO_2 nanoparticles***" (Submitted to Applied Materials & Interfaces)
5. Hafiz Mudaser Ahmad, Muhammad Shahzad Kamal, Mamdouh Al-Harthi "***Recent advances for inhibiting shale hydration in drilling oil and gas wells: A review***" (Submitted to Renewable and Sustainable Energy Reviews)

Conference Proceedings

1. Hafiz Mudaser Ahmad, Muhammad Shahzad Kamal, Mamdouh Al-Harthi, Mobeen Murtaza "***Improving the Drilling Fluid Properties using Nanoparticles and Water-Soluble Polymers***". Annual Technical Symposium and Exhibition (ATS&E), 2017. Society of Petroleum Engineers (SPE) Kingdom of Saudi Arabia. doi.org/10.2118/188140-MS
2. Hafiz Mudaser Ahmad, Muhammad Shahzad Kamal, Mamdouh Al-Harthi "***Assessment of Rheological and Filtration Properties of High molecular weight polymers in Bentonite Suspension as Drilling Fluids***". Middle East Process Engineering Conference & Exhibition at Kingdom of Bahrain 2017
3. Hafiz Mudaser Ahmad, Muhammad Shahzad Kamal, Mamdouh Al-Harthi "***Rheological Properties of Smart drilling fluids***" The 4th International Conference and Exhibition on Laboratory Technology, Kingdom of Bahrain, 2017
4. Hafiz Mudaser Ahmad, Muhammad Shahzad Kamal, Mamdouh Al-Harthi "***Formulation of drilling fluid: Effect of high molecular weight polymers and nano-particles***" 8th University Student Forum Conference (USFC), King Fahd University of Petroleum and Minerals (KFUPM), 2017.
5. Hafiz Mudaser Ahmad, Muhammad Shahzad Kamal, Mamdouh Al-Harthi "***Mitigation of Unconventional Reservoirs Instability and Formation Damage Problems using High Performance Drilling Fluids***" Annual Technical Symposium and Exhibition (ATS&E), 2018. Society of Petroleum Engineers (SPE) Kingdom of Saudi Arabia. (Submitted)

6. Hafiz Mudaser Ahmad, Muhammad Shahzad Kamal, Mamdouh Al-Harthi "***Synthesis and Experimental Investigation of Novel CNT-Polymer Nanocomposite to Enhance Borehole Stability at High Temperature Drilling Applications***" Annual Technical Symposium and Exhibition (ATS&E), 2018. Society of Petroleum Engineers (SPE) Kingdom of Saudi Arabia. (Submitted)
7. Hafiz Mudaser Ahmad, Muhammad Shahzad Kamal, Mamdouh Al-Harthi "***Enhancing wellbore stability of shale using novel polymer nanocomposite***" 9th University Student Forum Conference (USFC), King Fahd University of Petroleum and Minerals (KFUPM), 2018. (Submitted)